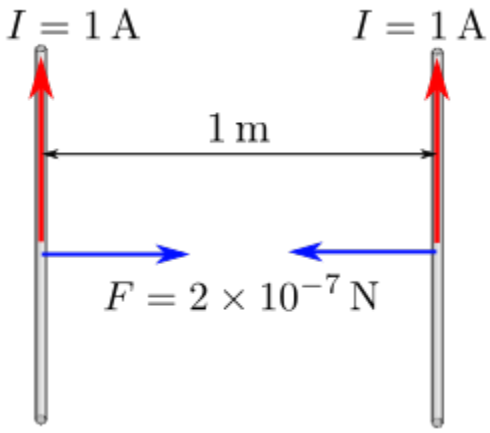
1.1 The original "International Ampere" was defined electrochemically as the current required to deposit 1.118 mg of silver per second from a solution of silver nitrate. Using this definition, how does the international ampere compare to the SI version? (Note that the SI version is based on the Ampere force law).

$$\frac{1.118\times10^{-3}\text{g Ag}}{\text{s}}\left|\frac{\text{mol Ag}}{107.8682\text{ g Ag}}\right|\frac{96485.33\text{ C}}{\text{equivalent}}\left|\frac{1\text{ equivalent}}{\text{mol Ag}}\right.=1.00022\text{ A}$$

The international Ampere is slightly larger than the SI one, which is the current required to create a force of 2×10^{-7} N for two parallel wires separated by a distance of 1 m.



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Chapter 1, problem 2

deposition of Mo from molten salt

MW = 95.94 [g/mol]

F = 96485 [coulomb/mol]

m = 12.85 [g]

I = 7 [coulomb/s]

t = 3600 [s]

$$m = I \cdot t \cdot \frac{MW}{F \cdot z}$$

z=1.95

SOLUTION

Unit Settings: SI C kPa kJ mass deg

F = 96485 [coulomb/mol]
m = 12.85 [g]
t = 3600 [s]
I = 7 [coulomb/s]
MW = 95.94 [g/mol]
z = 1.95

No unit problems were detected.

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Chapter 1, problem 3

amount of hydrogen needed to run fuel cell

F = 96485 [coulomb/mol]

Power = 50000 [W]

V = 0.7 [V] *cell voltage*

Power = I · V

t = 3600 · 3 · 1 [s]

MW = 0.002 [kg/mol] *molecular weight of hydrogen*

n = 2

$$m = I \cdot t \cdot \frac{MW}{F \cdot n}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

F = 96485 [coulomb/mol]
m = 7.995 [kg]
n = 2
t = 10800 [s]

I = 71429 [coulomb/s]
MW = 0.002 [kg/mol]
Power = 50000 [W]
V = 0.7 [V]

No unit problems were detected.

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Chapter 1, problem 4

Al production from Electrolysis

MW = 26.982 [g/mol]

F = 96485 [coulomb/mol]

I = 200000 [coulomb/s]

t = 24 · 3600 [s]

η = 0.95

$$m = \eta \cdot I \cdot t \cdot \frac{MW}{F \cdot z}$$

z = 3

cf1 = 1000 [g/kg]

$$prod_{rate} = \frac{m}{cf1}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cf1 = 1000 [g/kg]
F = 96485 [coulomb/mol]
m = 1.530E+06 [g]
$prod_{rate}$ = 1530 [kg]
z = 3

η = 0.95
I = 200000 [coulomb/s]
MW = 26.98 [g/mol]
t = 86400 [s]

No unit problems were detected.

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"!Chapter 1, problem 5"

"Power for Chlor-alkali process"

MW=70.9052[g/mol]; "molecular weight of Cl2"

F=96485 [coulomb/mol]

m=I*MW/(F*z)

z=2

cf1=24*365*3600 [s/year]

prod_rate=45e12 [g/year]

m=prod_rate/cf1

V=3.4 [V]

P=I*V

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cf1 = 3.154E+07 [s/year]	F = 96485 [coulomb/mol]
I = 3.883E+09 [coulomb/s]	m = 1.427E+06 [g/s]
MW = 70.91 [g/mol]	P = 1.320E+10 [W]
$prod_{rate}$ = 4.500E+13 [g/year]	V = 3.4 [V]
z = 2	

No unit problems were detected.

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"!Chapter 1, problem 6"

"deposition of Fe from molten salt"

MW=55.845[g/mol]

F=96485 [coulomb/mol]

m=50 [g]

I=25 [coulomb/s]

m=I*t*MW/(F*z)

z=3

"calculate the volume of chlorine gas"
MWg=70.9052 [g/mol]
R=8.314 [J/mol-K]
Tk=273 [K]
p=1e5 [N/m^2]

"from stoichiometry, get moles of Cl2"

n=(m/MW)*(3/2)

p*V=n*R*Tk

SOLUTION

Unit Settings: SI C kPa kJ mass deg

F = 96485 [coulomb/mol]	I = 25 [coulomb/s]
m = 50 [g]	MW = 55.85 [g/mol]
MWg = 70.91 [g/mol]	n = 1.343 [mol]
p = 100000 [N/m^2]	R = 8.314 [J/mol-K]
t = 10366 [s]	Tk = 273 [K]
V = 0.03048 [m^3]	z = 3

No unit problems were detected.

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"!Chapter 1, problem 7"

"Al production from Electrolysis"

MW=26.982[g/mol]

F=96485 [coulomb/mol]

I=150000 [coulomb/s]
t=24*(3600 [s])

eta=0.89

m=eta*I*t*MW/(F*z)

z=3

cf1=1000 [g/kg]

prod_rate=m/cf1

SOLUTION
Unit Settings: SI C kPa kJ mass deg

cf1 = 1000 [g/kg]	η = 0.89
F = 96485 [coulomb/mol]	I = 150000 [coulomb/s]
m = 1.075E+06 [g]	MW = 26.98 [g/mol]
$prod_{rate}$ = 1075 [kg]	t = 86400 [s]
z = 3	

No unit problems were detected.

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```
"!Chapter 1, problem 8"

"Electrodeposition of copper"
"use a basis of 1 m2"
A=1 [m^2]

MW=0.063546[kg/mol]
rho=8930 [kg/m^3]

F=96485 [coulomb/mol]


cd=1750 [A/m^2]
I=cd*A
loading=1.22 [kg/m^2]
m=loading*A
angle=165/360

d=loading/rho; "desired thickness of deposit"

eta=0.95

m=eta*I*t*MW/(F*z)

z=2
cf=3600 [s/h]

t=angle*cf/rotationrate
```

SOLUTION

Unit Settings: SI C kPa kJ mass deg

A = 1 [m^2]	angle = 0.4583
cd = 1750 [A/m^2]	cf = 3600 [s/h]
d = 0.0001366 [m]	η = 0.95
F = 96485 [coulomb/mol]	I = 1750 [coulomb/s]
loading = 1.22 [kg/m^2]	m = 1.22 [kg]
MW = 0.06355 [kg/mol]	ρ = 8930 [kg/m^3]
rotationrate = 0.7404 [1/h]	t = 2228 [s]
z = 2	

No unit problems were detected.

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Chapter 1, problem 9

amount of lithium in battery

MW = 6.941 [g/mol] *molecular weight of Li*

Cap = 1.32 [A-h]

cf1 = 3600 [coulomb/A-h]

F = 96485 [coulomb/mol]

$$m = Cap \cdot cf1 \cdot \frac{MW}{F \cdot z}$$

z = 1

SOLUTION

Unit Settings: SI C kPa kJ mass deg

Cap = 1.32 [A-h]
cf1 = 3600 [coulomb/A-h]
F = 96485 [coulomb/mol]
m = 0.3419 [g]
MW = 6.941 [g/mol]
z = 1

No unit problems were detected.

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problem 1-10

corrosion of steel plate

$m = 50$ [g]

$n = 2$

$F = 96485.33$ [Coulomb/mol]

$$m = I \cdot t \cdot \frac{MW}{n \cdot F}$$

$t = 3600 \cdot 24 \cdot 365$ [s]

$MW = 55.845$ [g/mol]

SOLUTION

Unit Settings: SI C kPa kJ mass deg

F = 96485 [Coulomb/mol]
m = 50 [g]
n = 2
I = 0.005479 [A]
MW = 55.85 [g/mol]
t = 3.154E+07 [s]

No unit problems were detected.

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PROBLEM 1-11

accelerated corrosion

$i = 0.14$ [A/m^2]

$n = 2$

$F = 96485.33$ [Coulomb/mol]

$$m = i \cdot t \cdot A \cdot \frac{MW}{n \cdot F}$$

$t = 360000$ [s]

$A = 0.01$ [m^2]

$MW = 55.845$ [g/mol] *molecular weight of iron*

$mr = 0.11$ [g]

$$\eta = \frac{mr}{m}$$ *faradaic efficiency*

$cur = i \cdot A$

oxygen evolved

$n1 = 4$

$$mo = i \cdot t \cdot A \cdot \left[\frac{1 - \eta}{n1 \cdot F}\right]$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

A = 0.01 [m^2]
η = 0.7542
i = 0.14 [A/m^2]
mo = 0.000321 [mol]
MW = 55.85 [g/mol]
n1 = 4
cur = 0.0014 [A]
F = 96485 [Coulomb/mol]
m = 0.1459 [g]
mr = 0.11 [g]
n = 2
t = 360000 [s]

No unit problems were detected.

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"!PROBLEM 1-12"

r= 1e-9 [m]

eo=8.854e-12 [farad/m]

q=1.602e-19 [coulomb]

W=q*q/(4*pi*eo*r)

phi=W/q

SOLUTION

Unit Settings: SI C kPa kJ mass deg

eo = 8.854E-12 [farad/m]
q = 1.602E-19 [coulomb]
W = 2.307E-19 [J]
ϕ = 1.44 [V]
r = 1.000E-09 [m]

No unit problems were detected.

2.1 Write the associated electrochemical reactions and calculate the standard potential, U^{θ} from ΔG^{o} for the following cells

a. Chlor-alkali process to produce hydrogen and chlorine from a brine of NaCl (aqueous salt solution). Use the hydrogen reaction for an alkaline solution.
b. Acetic acid/oxygen fuel cell with acidic electrolyte, where the acetic acid reacts to form liquid water and carbon dioxide. The reaction at the negative electrode is

$$2H_2O + CH_3COOH \rightarrow 2CO_2 + 8H^+ + 8e^-$$

a)

$$Cl_2 + 2e^- \leftrightarrow 2Cl^-$$
$$H_2 + 2OH^- \leftrightarrow 2H_2O + 2e^-$$

overall

$$H_2 + Cl_2 + 2NaOH \leftrightarrow 2H_2O + 2NaCl$$

$$\Delta G_{Rx} = \Delta G_f^{\text{products}} - \Delta G_f^{\text{reactants}}$$

$$\Delta G_{Rx}^o = 2\Delta G_{f,\text{NaCl}}^o + 2\Delta G_{f,\text{H2O}}^o - 2\Delta G_{f,\text{NaOH}}^o$$

$$\Delta G_{Rx}^o = 2\{-393.1 - 237.19 - (-419.2)\} = -422.34 \text{ kJ mol}^{-1}$$

$$U^{\theta} = \frac{-\Delta G_{Rx}^o}{nF} = \frac{4223440}{(2)96485} = 2.188 \text{ V}$$

b) multiply second reaction by 2 to balance electrons and add together

$$2H_2O + CH_3COOH \rightarrow 2CO_2 + 8H^+ + 8e^-$$
$$4H^+ + 4e^- + O_2 \leftrightarrow 2H_2O$$

overall

$$CH_3COOH + 2O_2 \leftrightarrow 2CO_2 + 2H_2O$$

$$\Delta G_{Rx}^o = 2\Delta G_{f,\text{CO2}}^o + 2\Delta G_{f,\text{H2O}}^o - \Delta G_{f,\text{CH3COOH}}^o$$

$$\Delta G_{Rx}^o = \{-(2)394.39 - (2)237.19 - (-389)\} = -874.18 \text{ kJ mol}^{-1}$$

$$U^{\theta} = \frac{-\Delta G_{Rx}^o}{nF} = \frac{874180}{(8)96485} = 1.113 \text{ V}$$

Does the redox reaction as written below proceed spontaneously at 25 °C and standard conditions?

$$2Ag^+ + H_2 \rightarrow 2Ag + 2H^+$$

$$Ag^+ + e^- \leftrightarrow Ag \qquad (U^\theta = 0.7991 \text{ V})$$

$$\tfrac{1}{2}H_2 \leftrightarrow H^+ + e^- \qquad (U^\theta = 0 \text{ V})$$

overall

$$Ag^+ + \tfrac{1}{2}H_2 \rightarrow Ag + H^+ \qquad (U = 0.7991 \text{ V})$$

$$U^\theta = \frac{-\Delta G^o_{Rx}}{nF} = 0.7991 \text{ V}$$

Thus, ΔG is less than zero, and the reaction would proceed spontaneously as written at standard conditions.

What is the standard half-cell potential for the oxidation of methane under acidic conditions? The reaction for methane is as follows:

$$\mathrm{CH_4(g) + 2H_2O(\ell) \rightarrow CO_2 + 8H^+ + 8e^-}$$

Which element is oxidized and how does its oxidation state change?

$$\mathrm{CH_4(g) + 2H_2O(\ell) \rightarrow CO_2 + 8H^+ + 8e^-} \qquad (U^{\theta}=? \text{ V})$$

$$\mathrm{8H^+ + 8e^- \leftrightarrow 4H_2} \qquad (U^{\theta}=0 \text{ V})$$

overall

$$\mathrm{CH_4(g) + 2H_2O(\ell) \rightarrow CO_2 + 4H_2}$$

Find the change in standard Gibbs energy of formation for the overall reaction

$$\Delta G^o_{Rx} = \Delta G^o_{f,\mathrm{CO2}} - 2\Delta G^o_{f,\mathrm{H2O}} - \Delta G^o_{f,\mathrm{CH4}}$$

$$\Delta G^o_{Rx} = \{-394.359 - 2(-237.19) - (-50.5)\} = -130.52 \text{ kJ mol}^{-1}$$

$$U^{\theta} = \frac{-\Delta G^o_{Rx}}{nF} = \frac{130520}{8F} = 0.1691 \text{ V}$$

The oxidation state of carbon changes.

What is the standard cell potential for a methane /oxygen fuel cell? The oxidation of methane produces CO_2 as shown in problem 2.3, but here assume the product water is a gas, rather than a liquid.

$$\mathrm{CH_4(g) + 2H_2O(g) \rightarrow CO_2 + 8H^+ + 8e^-} \qquad (U^\theta = ?\ \mathrm{V})$$

$$\mathrm{8H^+ + 8e^- + 2O_2 \leftrightarrow 4H_2O(g)} \qquad (U^\theta = 0\ \mathrm{V})$$

overall

$$\mathrm{CH_4(g) + 2O_2 \rightarrow CO_2 + 2H_2O(g}$$

Find the change in standard Gibbs energy of formation for the overall reaction

$$\Delta G^o_{Rx} = \Delta G^o_{f,\mathrm{CO2}} + 2\Delta G^o_{f,\mathrm{H2O}} - \Delta G^o_{f,\mathrm{CH4}}$$

$$\Delta G^o_{Rx} = \{-394.359 + 2(-228.572) - (-50.5)\} = -801\ \mathrm{kJ\ mol^{-1}}$$

$$U^\theta = \frac{-\Delta G^o_{Rx}}{nF} = \frac{801000}{8F} = 1.038\ \mathrm{V}$$

Let's consider the oxidation of methane in a fuel cell that utilizes an oxygen conductor (O^{2-}) rather than a proton conductor as the electrolyte.

a. At which electrode (oxygen or methane) is O^{2-} produced and at which is it consumed?
b. In which direction does O^{2-} move through the electrolyte? Why?
c. Propose two electrochemical half-cell reactions.
d. Does U^{θ} change for this fuel cell relative to a fuel cell that utilizes a proton conductor? Why or why not?

a. O^{2-} is produced at the cathode; and O^{2-} is consumed at the anode

$$O_2 + 4\,e^- \rightarrow 2O^{2-}$$

b. oxygen ions move from the cathode to the anode, since they are negatively charged this still represents a positive current from the anode to the cathode.

c.

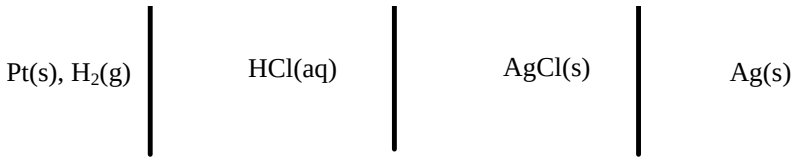
$$CH_4(g) + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$
$$2O_2 + 8\,e^- \rightarrow 4O^{2-}$$

overall

$$CH_4(g) + 2O_2 \rightarrow CO_2 + 2H_2O(g)$$

d. No, the standard potential depends on the overall reaction and the reference pressure, but since the overall reaction is the same regardless of the ion conductor.

Determine the equilibrium potential of the cell shown below.



The reaction at positive electrode (right) is

$$\mathrm{AgCl} + \mathrm{e}^- \leftrightarrow \mathrm{Ag} + \mathrm{Cl}^- \qquad U^\theta = 0.222\ \mathrm{V}$$

and for the negative (left)

$$\mathrm{H_2} \leftrightarrow 2\mathrm{H}^+ + 2\mathrm{e}^- \qquad U^\theta = 0$$

overall

$$\mathrm{H_2} + 2\mathrm{AgCl} \leftrightarrow 2\mathrm{Ag} + 2\mathrm{HCl} \qquad U^\theta = 0.222\ \mathrm{V}$$

where the overall potential for the cell is the positive (right) – negative (left).

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{nF} \ln \prod a_i{}^{s_i}, \tag{2-11}$$

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{nF} \ln \frac{a_{\mathrm{Ag}}^2 a_{\mathrm{HCl}}^2}{a_{\mathrm{H2}} a_{\mathrm{AgCl}}^2},$$

The activity of solids are assumed to be one, and n=2

$$U = U^\theta{}_{\text{cell}} + \frac{RT}{2F} \ln a_{\mathrm{H2}} - \frac{RT}{F} \ln a_{\mathrm{HCl}},$$

Hydrogen is a gas, assume ideal

$$a_{\mathrm{H2}} = \frac{f_{\mathrm{H2}}}{f^o} = \frac{p_{\mathrm{H2}}}{p^o}$$

For the aqueous HCl

$$a_{\mathrm{HCl}} = a_+^{\nu+} a_-^{\nu-} = m_+ \gamma_+ m_- \gamma_- = m^2 \gamma_\pm^2$$

substituting gives

$$\boxed{U = U^\theta{}_{\text{cell}} + \frac{RT}{2F} \ln\left(\frac{p_{\mathrm{H2}}}{p^o}\right) - \frac{2RT}{F} \ln\left(m\gamma_\pm\right)}$$

Consider the electrochemical reactions shown below. Mercury(I) chloride, also known as *calomel*, is a solid used in reference electrodes. The two reactions are

$$Zn \leftrightarrow Zn^{2+} + 2e^-$$

$$Hg_2Cl_2 + 2e^- \leftrightarrow 2Cl^- + 2Hg$$

a. What is the overall chemical reaction?
b. Develop an expression for *U*, the equilibrium potential of the cell.
c. Write down an expression for the standard potential of the cell in terms of the standard Gibbs energies of formation.
d. Use standard half-cell potentials from the table to determine the standard Gibbs energy of formation for aqueous $ZnCl_2$. Why is this value different than the value for solid $ZnCl_2$?
e. What is the standard Gibbs energy of formation for Hg_2Cl_2?

a) The reaction at positive electrode is

$$Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^- \qquad U^\theta = 0.2676 \text{ V}$$

and for the negative

$$Zn \leftrightarrow Zn^{2+} + 2e^- \qquad U^\theta = -0.7618 \text{ V}$$

overall

$$Hg_2Cl_2 + Zn \leftrightarrow 2Hg + Zn^{2+} + 2Cl^- \qquad U^\theta = 1.029 \text{ V}$$

b)

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{nF} \ln \prod a_i{}^{s_i}, \tag{2-11}$$

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{nF} \ln \frac{a_{\text{Hg}}^2 a_{\text{ZnCl2}}}{a_{\text{Zn}} a_{\text{Hg}_2\text{Cl}_2}},$$

The activity of solid and liquid Hg are assumed to be one, and n=2

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{2F} \ln a_{\text{ZnCl}_2},$$

ν_+=1, ν_-=2, ν=3
For the aqueous $ZnCl_2$

$$a_{\text{ZnCl}_2} = a_+^{\nu+} a_-^{\nu-} = m_+ \gamma_+ m_-^2 \gamma_-^2 = 4m^3 \gamma_\pm^3$$

substituting gives

$$\boxed{U = U^\theta{}_{\text{cell}} - \frac{RT}{F} \ln 2 - \frac{3RT}{2F} \ln\left(m\gamma_\pm\right)}$$

c,d) From the table of standard potentials

$$\mathrm{Cl_2 + 2e^- \leftrightarrow 2Cl^-} \qquad U^{\theta}=1.3595\text{V}$$
$$\mathrm{Zn \leftrightarrow Zn^{2+} + 2e^-} \qquad U^{\theta}=-0.7618\text{ V}$$

Given that the solids and liquids are in their standard state, we can right the change in Gibbs energy as

$$\Delta G^o_{Rx} = \Delta G^o_{f,\mathrm{ZnCl2}} = -nFU^{\theta} = -2(96485)(2.121\ V) = -409.3\text{ kJ}$$

e)

$$\mathrm{Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-} \qquad U^{\theta}=0.2676\text{ V}$$
$$\mathrm{Zn \leftrightarrow Zn^{2+} + 2e^-} \qquad U^{\theta}=-0.7618\text{ V}$$

$$\mathrm{Zn + Hg_2Cl_2 \leftrightarrow ZnCl_2(aq) + 2Hg} \qquad U^{\theta}=1.029\text{V}$$

$$\Delta G^o_{Rx} = -nFU^{\theta} = -198{,}740\text{ J mol}^{-1}$$

$$\Delta G^o_{Rx} = \Delta G^o_{f,\mathrm{ZnCl2}} - \Delta G^o_{f,\mathrm{Hg2Cl2}} = -210.6\text{ kJ mol}^{-1}$$

The values are different because the standard states are different for a solid versus solution. There is some change in energy and entropy involved in the dissolution of the solid.

The lithium air cell offers the possibility of a very high energy battery. At the negative electrode,

$$\mathrm{Li} \leftrightarrow \mathrm{Li^+} + \mathrm{e^-}$$

.

At the positive electrodes the following reactions are postulated

$$2\mathrm{Li^+} + \mathrm{O_2} + 2\mathrm{e^-} \leftrightarrow \mathrm{Li_2O_2}\,.$$

$$2\mathrm{Li^+} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{e^-} \leftrightarrow \mathrm{Li_2O}\,.$$

Estimate the standard potential for each of the two possible reactions at the positive electrode paired with a lithium anode.

The reaction at positive electrode is

$$2\mathrm{Li^+} + \mathrm{O_2} + 2\mathrm{e^-} \leftrightarrow 2\mathrm{Li_2O_2}$$

and for the negative

$$2\mathrm{Li} \leftrightarrow 2\mathrm{Li^+} + 2\mathrm{e^-}$$

---

overall

$$2\mathrm{Li} + \mathrm{O_2} \leftrightarrow 2\mathrm{Li_2O_2}$$

$$\Delta G^o_{Rx} = \Delta G^o_{f,\mathrm{Li2O2}} = -571.116\ \mathrm{kJ} = -nFU^\theta$$

$$U^\theta = \frac{-\Delta G^o_{Rx}}{nF} = \frac{-571116}{2F} = \boxed{2.96\ \mathrm{V}}$$

For the second reaction, at the positive electrode is

$$2\mathrm{Li^+} + \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{e^-} \leftrightarrow \mathrm{Li_2O}$$

and for the negative

$$2\mathrm{Li} \leftrightarrow 2\mathrm{Li^+} + 2\mathrm{e^-}$$

---

overall

$$2\mathrm{Li} + \tfrac{1}{2}\mathrm{O_2} \leftrightarrow \mathrm{Li_2O}$$

$$\Delta G^o_{Rx} = \Delta G^o_{f,\mathrm{Li2O}} = -561.2\ \mathrm{kJ} = -nFU^\theta$$

$$U^\theta = \frac{-\Delta G^o_{Rx}}{nF} = \frac{-571200}{2F} = \boxed{2.91\ \mathrm{V}}$$

Develop an expression for the equilibrium potential for the cell below. The first reaction is the negative electrode of the Edison cell (battery).

$$\mathrm{Fe} + 2\mathrm{OH}^- \rightarrow \mathrm{Fe(OH)_2} + 2e^-$$
$$\mathrm{O_2} + 4\mathrm{e}^- + 2\mathrm{H_2O} \rightarrow 4\mathrm{OH}^-$$

The Gibbs energy of formation for $Fe(OH)_2$ is -486.6 kJ/mol.

The reaction at positive electrode is

$$\mathrm{O_2} + 4\mathrm{e}^- + 2\mathrm{H_2O} \leftrightarrow 4\mathrm{OH}^- \qquad U^{\theta}=0.401\ \mathrm{V}$$

and for the negative

$$\mathrm{Fe} + 2\mathrm{OH}^- \rightarrow \mathrm{Fe(OH)_2} + 2\mathrm{e}^- \qquad U^{\theta}=?$$

overall

$$2\mathrm{Fe} + \mathrm{O_2} + 2\mathrm{H_2O} \leftrightarrow \mathrm{Fe(OH)_2}$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{nF}\ln\prod a_i{}^{s_i}, \qquad (2\text{-}11)$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{nF}\ln\frac{a^2_{\mathrm{Fe(OH)_2}}}{a^2_{\mathrm{Fe}}a_{\mathrm{O2}}a^2_{\mathrm{H_2O}}},$$

$$U = U^{\theta}{}_{\text{cell}} + \frac{RT}{2F}\ln a_{\mathrm{H_2O}} + \frac{RT}{4F}\ln\left(\frac{p_{O2}}{p^o}\right)$$

$$U^{\theta} = \frac{-\Delta G^o_{Rx}}{nF}$$

$$\Delta G^o_{Rx} = 2\Delta G^o_{f,\mathrm{Fe(OH)_2}} - 2\Delta G^o_{\mathrm{H_2O}} = 2\{-486{,}600 - (-237{,}2 = 129)\} = -499.5\ \mathrm{kJ\ mol^{-1}}$$

$$U^{\theta} = \frac{-\Delta G^o_{Rx}}{nF} = \frac{499500}{(4)96485} = 1.29\ \mathrm{V}$$

$$\boxed{U = 1.29 + \frac{RT}{2F}\ln a_{\mathrm{H_2O}} + \frac{RT}{4F}\ln\left(\frac{p_{O2}}{p^o}\right)}$$

Develop an expression for the equilibrium potential of a hydrogen-oxygen fuel cell operating under acidic conditions. The two electrochemical reactions are

$$H_2 \leftrightarrow 2H^+ + 2e^- \qquad \text{and} \qquad O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$$

Use the data in the Appendix C for standard Gibbs energy of formation. Compare with the value calculated from standard electrode potentials to identify whether the standard state for water in the table of Appendix A is liquid or gas.

The reaction at positive electrode is

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \qquad U^\theta = 1.229 \text{ V}$$

and for the negative

$$H_2 \leftrightarrow 2H^+ + 2e^- \qquad U^\theta = 0 \text{ V}$$

overall

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$$

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{nF}\ln\prod a_i{}^{s_i}, \tag{2-11}$$

$$U = U^\theta{}_{\text{cell}} + \frac{RT}{nF}\ln\frac{a_{O_2}^{1/2}a_{H_2}}{a_{H_2O}},$$

$$U = U^\theta{}_{\text{cell}} + \frac{RT}{2F}\ln\frac{\left(\frac{p_{H_2}}{p^o}\right)\left(\frac{p_{O_2}}{p^o}\right)^{0.5}}{a_{H_2O}}$$

$$U^\theta = \frac{-\Delta G^o_{Rx}}{nF} = 1.229 \text{ V, where } n=2$$

Therefore, $\Delta G^o_{Rx} = -nFU^\theta = -2(96485)1.229 = -237 \text{ kJ mol}^{-1}$

From the Appendix C

liquid $\Delta G^o_{f,H2O} = -237 \text{ kJ mol}^{-1}$

gas $\Delta G^o_{f,H2O} = -229 \text{ kJ mol}^{-1}$

Thus, the 1.229 V corresponds to liquid water

Write the associated electrochemical reactions, and calculate the standard potential, U^0, from ΔG^o for the following cells

a. Propane fuel cell with solid oxygen conductor electrolyte
b. Electrolysis of aluminum, where aluminum is produced from Al_2O_3 and carbon. Note that carbon is oxidized at the anode.

a) The reaction at positive electrode is

$$5O_2 + 20e^- \leftrightarrow 10O^{2-}$$

and for the negative

$$C_3H_8 + 10O^{2-} \leftrightarrow 3CO_2 + 4H_2O + 20e^-$$

overall

$$C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$$

Since the oxygen ion does not appear in the overall reaction, the standard potential does not depend on its activity.

$$\Delta G^o_{Rx} = -nFU^\theta = 3\Delta G^o_{f,CO2} + 4\Delta G^o_{f,H2O} - \Delta G^o_{f,C3H8}$$

$$\Delta G^o_{Rx} = -nFU^\theta = 3(-394.3) + 4(-228.6) - (-24.3) = -2070 \text{ kJ mol}^{-1}$$

$$U^\theta = \frac{-2{,}070{,}000}{20F} = 1.074 \text{ V}$$

b) The overall reaction is

$$2Al_2O_3 + 3C \leftrightarrow 4Al + 3CO_2$$

.

$$\Delta G^o_{Rx} = -nFU^\theta = 3\Delta G^o_{f,CO2} - 2\Delta G^o_{f,Al2O3}$$

$$\Delta G^o_{Rx} = -nFU^\theta = 3(-394.3) - 2(-1582.3)$$

$$U^\theta = \frac{-1{,}981{,}500}{12F} = 1.711 \text{ V}$$

The actual reactions are complex, here is one set of reactions

$$3C + 6O^{2-} \leftrightarrow 3CO_2 + 12e^-$$
$$2Al_2O_3 + 12e^- \leftrightarrow 4Al + 6O^{2-}$$

Calculate the equilibrium potential for peroxide formation in an acid fuel cell

$$O_2 + 2H^+ + 2e^- \rightarrow H_2$$

The reaction at positive electrode is

$$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2$$

and for the negative

$$H_2 \leftrightarrow 2H^+ + 2e^- \qquad U^{\theta}=0 \text{ V}$$

overall

$$H_2 + O_2 \leftrightarrow H_2O_2$$

Therefore for liquid peroxide

$$\Delta G^o_{Rx} = \Delta G^o_{f,H2O2} = -120.42 \text{ kJ mol}^{-1}$$

$$U^{\theta}{}_{\text{cell}} = \frac{-\Delta G^o_{Rx}}{nF} = \frac{120{,}420}{2\,F} = 0.624 \text{ V}$$

Alternatively, if peroxide is formed as an aqueous solution

$$\Delta G^o_{Rx} = \Delta G^o_{f,H2O2} = -134.1 \text{ kJ mol}^{-1}$$

$$U^{\theta}{}_{\text{cell}} = \frac{-\Delta G^o_{Rx}}{nF} = \frac{134{,}097}{2\,F} = 0.695 \text{ V}$$

From the Appendix C

liquid $\Delta G^o_{f,\text{H2O2}} = -120.4 \text{ kJ mol}^{-1}$

aqueous solution $\Delta G^o_{f,\text{H2O2}} = -134.1 \text{ kJ mol}^{-1}$

Value not in appendix

Use the half-cell reactions for the reduction of cupric ion (Cu^{2+}) to copper metal and cuprous ion (Cu^{+}) to copper metal to calculate the standard potential for the reduction of cupric ion to cuprous ion. Check your answer against the value given in Appendix A.

$$\begin{aligned} Cu^{2+} + 2e^- &\rightarrow Cu & U_1^\theta &= 0.337\ V \\ Cu^{+} + e^- &\rightarrow Cu & U_2^\theta &= 0.521\ V \end{aligned}$$

Subtract the second reaction from the first to get the desired reaction

$$Cu^{2+} + e^- \rightarrow Cu^{+}$$

Because the electrons per copper atom are not the same for the two reactions, we need to use the ΔG method, we can't just subtract the two standard potentials.

$$\Delta G_3^o = \Delta G_1^o - \Delta G_2^o$$

$$-FU_3^\theta = -2FU_1^\theta - \left(-FU_2^\theta\right)$$

$$U_3^\theta = 2(0.337) - (0.521) = \boxed{0.153\ V}$$

This is same value tabulated in Appendix A.

Consider the electrochemical cell below.

$$\text{Pt(s), } H_2\text{(g)} \;\big|\; \text{HCl(aq)} \;\big|\; \text{Pt(s), } Cl_2\text{(g)}$$

The two reactions are

$$H_2 \leftrightarrow 2H^+ + 2e^-$$
$$Cl_2 + 2e^- \leftrightarrow 2Cl^-$$

Find an expression for *U*. If the pressure of hydrogen is 250 kPa and that of chlorine is 150 kPa, what is the numerical value of *U* at 25 °C in one molal HCl? Include the simplified activity corrections (you may neglect activity coefficients).

The equilibrium potential for the chlorine reaction is 1.3595 V, which is the standard cell potential. The overall reaction is

$$Cl_2 + H_2 \leftrightarrow 2HCl(aq) \qquad n=2$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{nF}\ln\prod a_i{}^{s_i}, \tag{2-11}$$

$$U = U^{\theta}_{\text{cell}} - \frac{RT}{nF}\ln\frac{a^2_{\text{HCl}}}{a_{\text{H2}}a_{\text{Cl2}}},$$

$$U = 1.3595 - \frac{RT}{F}\ln a_{\text{HCl}} + \frac{RT}{2F}\ln\left(p_{\text{Cl2}}/p^o\right)\left(p_{\text{H2}}/p^o\right),$$

for a 1 molal solution, the activity is one assuming that $\gamma_{\pm}=1$

$$U = 1.3595 + \frac{RT}{2F}\ln\left(150/100\right)\left(250/100\right) = \boxed{1.376\text{ V}}$$

Create a Pourbaix diagram for Pb. Treat the following reactions

$$\mathrm{Pb} \leftrightarrow \mathrm{Pb}^{2+} + 2\mathrm{e}^- \quad \text{(c)}$$
$$\mathrm{Pb}^{2+} + \mathrm{H_2O} \leftrightarrow \mathrm{PbO} + 2\mathrm{H}^+ \quad \text{(d)}$$
$$\mathrm{Pb} + \mathrm{H_2O} \leftrightarrow \mathrm{PbO} + 2\mathrm{H}^+ + 2\mathrm{e}^- \quad \text{(e)}$$
$$\mathrm{Pb}^{2+} + 2\mathrm{H_2O} \leftrightarrow \mathrm{PbO_2} + 4\mathrm{H}^+ + 2\mathrm{e}^- \quad \text{(f)}$$
$$3\mathrm{PbO} + \mathrm{H_2O} \leftrightarrow \mathrm{Pb_3O_4} + 2\mathrm{H}^+ + 2\mathrm{e}^- \quad \text{(g)}$$

from text in Chapter 2

$$U_a = -\frac{RT}{2F}\ln\frac{1}{\left(\frac{c_{\mathrm{H}^+}}{c^o}\right)^2} = \frac{RT}{F}\ln\left(\frac{c_{\mathrm{H}^+}}{c^o}\right) = -\frac{RT}{F}2.303\ \mathrm{pH} = -0.0592\ \mathrm{pH} \quad \text{(a)}$$

$$U_b = U^\theta{}_{b/\mathrm{SHE}} - \frac{RT}{F}2.303\ \mathrm{pH} = 1.229 - 0.0592\ \mathrm{pH}, \quad \text{(b)}$$

For the first reaction, (c)

$$\mathrm{Pb} \leftrightarrow \mathrm{Pb}^{2+} + 2\mathrm{e}^-. \quad \text{(c)}$$

$$U_c = U^\theta{}_{c/\mathrm{SHE}} - \frac{RT}{nF}\ln\frac{c^o}{c_{\mathrm{Pb}^{2+}}}$$

$$U_c = -0.126 + 2.303\frac{RT}{2F}\log[\mathrm{Pb}^{2+}]$$

Assume the concentration of lead ion is 10^{-6} M,

$$U_c = -0.126 + 2.303\frac{RT}{2F}(-6) = -0.304\ \mathrm{V}$$

The second reaction (d) is a chemical equilibrium

$$K_{sp} = \frac{(a_{\mathrm{Pb}^{2+}})(a_{\mathrm{H_2O}})}{(a_{\mathrm{PbO}})(a_{\mathrm{H}^+}^2)} = e^{\frac{nFU^\theta}{RT}}$$

.

$a_{\mathrm{H_2O}} = a_{\mathrm{PbO}} = 1$, n=2

Obtain Gibbs energy of formation from Appendix C

$$\Delta G^o_{f,\mathrm{Pb}^{2+}} = -24.39\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta G^o_{f,\mathrm{PbO}} = -187.9\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta G^o_{f,\mathrm{H_2O}} = -237.129\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta G^o_{Rx} = (-187.9) - (-24.39) - (-237.129) = 73.619\ \mathrm{kJ}$$

$$U^{\theta} = \frac{-\Delta G_{Rx}^{o}}{nF} = \frac{73{,}619}{(2)96485} = 0.382\ \text{V}$$

$$K_{sp} = \frac{(a_{\text{Pb}^{2+}})}{\left(a_{\text{H}^{+}}^{2}\right)} = e^{\frac{nFU^{\theta}}{RT}} = 8.22 \times 10^{12}$$

$a_{\text{Pb}^{2+}} = 10^{-6}$, and $pH = \log(a_{\text{H}^{+}})$

$$a_{\text{H}^{+}}^{2} = \frac{10^{-6}}{8.22 \times 10^{12}}$$

$$a_{\text{H}^{+}} = 3.49 \times 10^{-10}$$

$$pH = \log(a_{\text{H}^{+}}) = 9.46$$

Reaction (e)

$$U_e = U^{\theta}{}_{d/\text{SHE}} - \frac{RT}{nF}\ln\frac{(a_{\text{Pb}})(a_{\text{H}_2\text{O}})}{\left(a_{\text{H}^{+}}^{2}\right)(a_{\text{PbO}})}$$

$a_{\text{PbO}} = a_{\text{Pb}} = a_{\text{H}_2\text{O}} = 1$

$$U_e = U^{\theta}{}_{e/\text{SHE}} + \frac{2.303RT}{F}\log\left(a_{\text{H}^{+}}\right) = U^{\theta}{}_{e/\text{SHE}} - \frac{2.303RT}{F}\text{pH}$$

Use Gibbs energy of formation to obtain the standard potential

$$\Delta G_{Rx}^{o} = (-237.129) - (-187.9) = -nFU_e^{\theta}$$

$$U_e^{\theta} = 0.255\ V$$

$$U_e = 0.255 - 0.0592\text{pH}$$

Reaction (f)

Use Gibbs energy of formation to obtain the standard potential

$$\Delta G_{Rx}^{o} = (-24.39) + 2(-237.129) - (-217.3) = -nFU_f^{\theta}$$

n=2,

$$U_f^{\theta} = \frac{-\Delta G_{Rx}^{o}}{nF} = 1.458\ V$$

$$U_f = U^{\theta}{}_{f/\text{SHE}} - \frac{RT}{nF}\ln\frac{(a_{\text{Pb}^{2+}})\left(a_{\text{H}_2\text{O}}^{2}\right)}{\left(a_{\text{H}^{+}}^{4}\right)(a_{\text{PbO}_2})}$$

$a_{\text{PbO}_2} = a_{\text{H}_2\text{O}} = 1$, and $a_{\text{Pb}^{2+}} = 10^{-6}$

$$U_f = U^{\theta}{}_{f/\mathrm{SHE}} - \frac{RT}{2F}\ln(10^{-6}) + \frac{2RT}{F}\ln(a_{\mathrm{H}^+})$$

$$U_f = 1.458 + 0.1775 + \frac{2RT}{F}\ln(a_{\mathrm{H}^+})$$

$$U_f = 1.6355 - 0.1183\mathrm{pH}$$

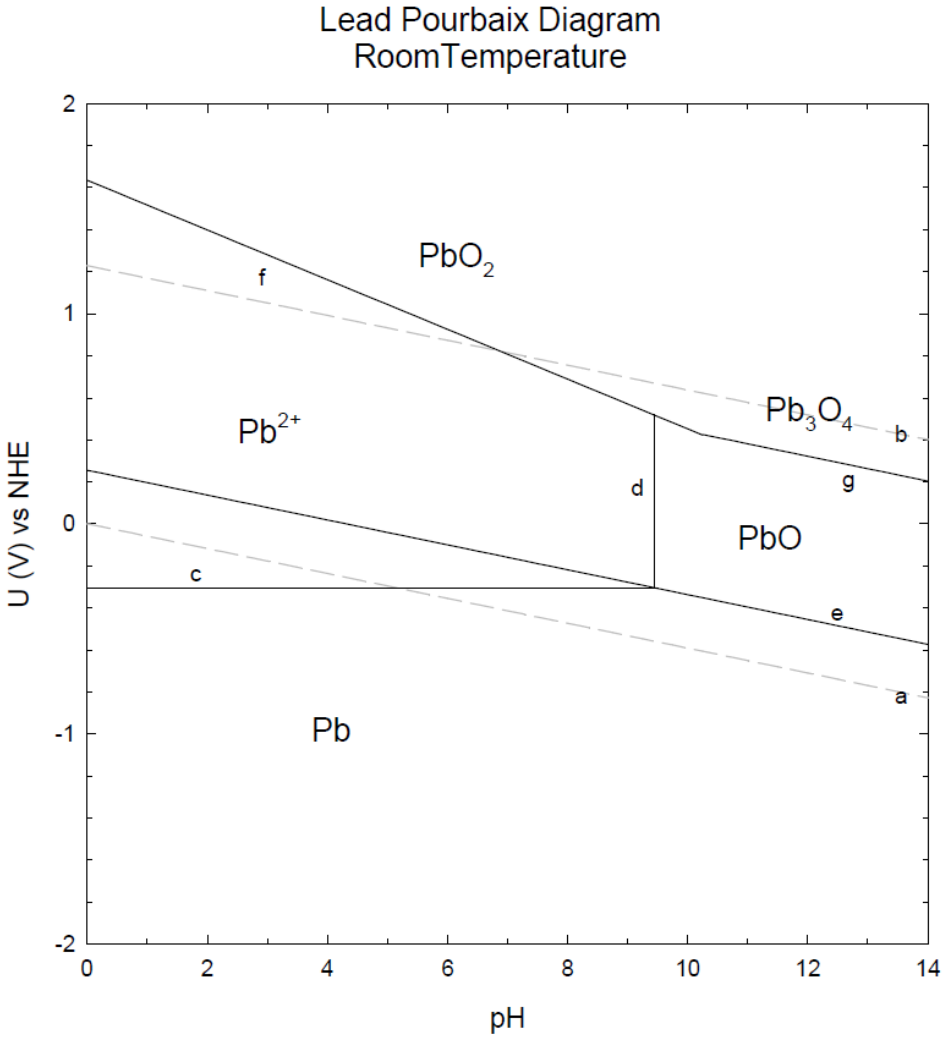
Reaction (g)

$$\Delta G^o_{Rx} = 3(-187.9) + (-237.129) - (-601.7) = -nFU^{\theta}_g$$

$$U^{\theta}_g = \frac{-\Delta G^o_{Rx}}{2F} = 1.032\ V$$

$$U_g = U^{\theta}_g + \frac{RT}{F2}\ln(a_{\mathrm{H}^+})$$

$$U_g = 1.032 - 0.0592\mathrm{pH}$$



Create a Pourbaix diagram for Pt. Focus on the low pH range (-2 ≤ pH ≤ 1), and consider the following reactions.

$Pt \leftrightarrow Pt^{2+} + 2e^-$	(1.188 V)	(c)
$Pt^{2+} + H_2O \leftrightarrow PtO + 2H^+$		(d)
$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^-$	(0.980 V)	(e)
$PtO + H_2O \leftrightarrow PtO_2 + 2H^+ + 2e^-$	(1.045 V)	(f)
$Pt^{2+} + 2H_2O \leftrightarrow PtO_2 + 4H^+ + 2e^-$	(0.837 V)	(g)

from text in Chapter 2

$$U_a = -\frac{RT}{2F}\ln\frac{1}{\left(\frac{c_{H^+}}{c^o}\right)^2} = \frac{RT}{F}\ln\left(\frac{c_{H^+}}{c^o}\right) = -\frac{RT}{F}2.303\ \text{pH} = -0.0592\ \text{pH} \qquad \text{(a)}$$

$$U_b = U^\theta{}_{b/\text{SHE}} - \frac{RT}{F}2.303\ \text{pH} = 1.229 - 0.0592\ \text{pH}, \qquad \text{(b)}$$

For the first reaction, (c)

$$Pt \leftrightarrow Pt^{2+} + 2e^-. \qquad \text{(c)}$$

$$U_c = U_c^\theta - \frac{RT}{nF}\ln\frac{c^o}{c_{Pt^{2+}}}$$

$$U_c = 1.188 + 2.303\frac{RT}{2F}\log[Pt^{2+}]$$

Assume the concentration of platinum ion is 10^{-6} M,

$$U_c = 1.011\ \text{V}$$

The second reaction (d) is a chemical equilibrium

$$K_{sp} = \frac{(a_{Pt^{2+}})(a_{H_2O})}{(a_{PtO})(a_{H^+}^2)} = \frac{(a_{Pt^{2+}})}{(a_{H^+}^2)} = e^{\frac{nFU^\theta}{RT}}$$

.

$a_{H_2O} = a_{PbO} = 1$, n=2

This equilibrium reaction (d) is the difference of

$$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^-$$

$$Pt \leftrightarrow Pt^{2+} + 2e^-$$

$$U^\theta = 0.980 - 1.188 = -0.208\ \text{V}$$

Using the equation above for Ksp and the definition of pH,

$$pH = \frac{1}{2}\left\{\frac{nFU^\theta}{2.303RT}\right\} - \log[Pt^{2+}] = -0.516$$

Reaction (e)

$$U_e = U_e^\theta + \frac{RT}{F}\ln(a_{\mathrm{H^+}})$$

$$U_e = 0.980 + 2.303\frac{RT}{F}\log(a_{\mathrm{H^+}})$$

$$U_e = 0.980 - 0.0592\ \mathrm{pH}$$

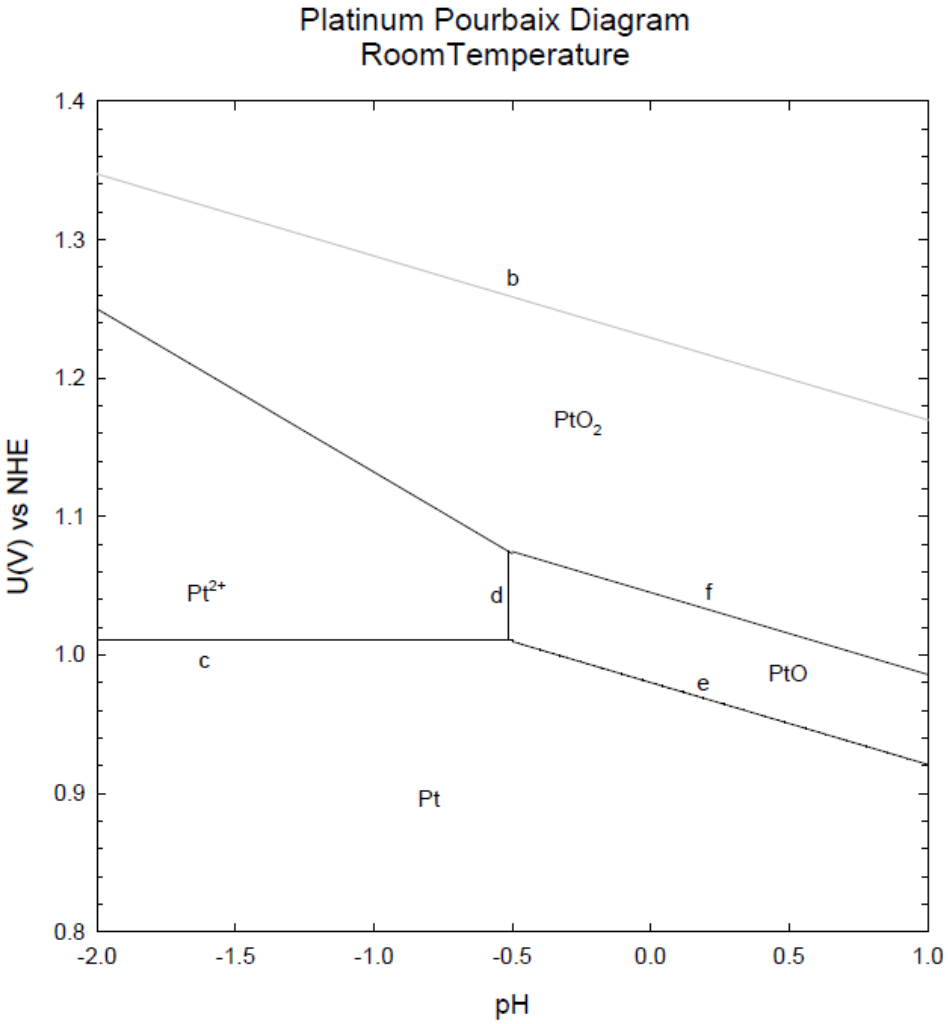
Reaction (f), same approach as for reaction (e)

$$U_f = 1.045 - 0.0592\ \mathrm{pH}$$

Reaction (g)

$$U_g = U_g^\theta - \frac{RT}{2F}\ln[10^{-6}] + 2.303\frac{4RT}{2F}\log(a_{\mathrm{H^+}})$$

$$U_g = 1.014 - 0.118\ \mathrm{pH}$$



Create a Pourbaix diagram for Fe. Treat the following reactions

$Fe^{2+} + 2e^- \leftrightarrow Fe.$	(-0.440 V)	(c)
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}.$	(0.771 V)	(d)
$Fe_3O_4 + 8H^+ + 8e^- \leftrightarrow 3Fe + 4H_2O$	(-0.085 V)	(e)
$Fe_3O_4 + 8H^+ + 2e^- \leftrightarrow 3Fe^{2+} + 4H_2O$	(0.980 V)	(f)
$Fe_2O_3 + 6H^+ + 2e^- \leftrightarrow 2Fe^{2+} + 3H_2O$	(0.728 V)	(g)
$2Fe^{3+} + 3H_2O \leftrightarrow Fe_2O_3 + 6H^+$		(h)
$3Fe_2O_3 + 2H^+ + 2e^- \leftrightarrow 2Fe_3O_4 + H_2O$	(0.221 V)	(i)
$Fe_3O_4 + H_2O + OH^- + 2e^- \leftrightarrow 3HFeO_2^-$	(-1.819 V)	(j)
$HFeO_2^- + 3H^+ + 2e^- \leftrightarrow Fe + 2H_2O$	(0.493 V)	(k)

from text in Chapter 2

$$U_a = -\frac{RT}{2F}\ln\frac{1}{\left(\frac{c_{H^+}}{c^o}\right)^2} = \frac{RT}{F}\ln\left(\frac{c_{H^+}}{c^o}\right) = -\frac{RT}{F}2.303\ \text{pH} = -0.0592\ \text{pH} \qquad \text{(a)}$$

$$U_b = U^\theta{}_{b/\text{SHE}} - \frac{RT}{F}2.303\ \text{pH} = 1.229 - 0.0592\ \text{pH}, \qquad \text{(b)}$$

For the first reaction, (c)

$$Fe^{2+} + 2e^- \leftrightarrow Fe. \qquad \text{(c)}$$

$$U_c = U_c^\theta - \frac{RT}{nF}\ln\frac{c^o}{c_{Pt^{2+}}}$$

$$U_c = -0.440 + 2.303\frac{RT}{2F}\log[Fe^{2+}]$$

Assume the concentration of iron ion is 10^{-6} M,

$$U_c = -0.6175\ \text{V}$$

For the second reaction, (d)

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+}. \qquad \text{(c)}$$

$$U_d = U_d^\theta - \frac{RT}{nF}\ln\frac{c_{Fe^{2+}}}{c_{Fe^{3+}}}$$

if the concentration of iron (II) and iron (III) are the same

$$U_d = U_d^\theta = 0.771\ \text{V}$$

Reaction (e) $Fe_3O_4 + 8H^+ + 8e^- \leftrightarrow 3Fe + 4H_2O$

$$U_e = U_e^\theta + \frac{RT}{F}\ln(a_{H^+})$$

$$U_e = -0.085 - 0.0592\ \text{pH}$$

Reaction (f), $Fe_3O_4 + 8H^+ + 2e^- \leftrightarrow 3Fe^{2+} + 4H_2O$

$$U_f = U_f^\theta - \frac{RT}{nF}\ln\frac{\left(a_{Fe^{2+}}^3\right)\left(a_{H_2O}^4\right)}{\left(a_{H^+}^8\right)}$$

$$U_f = U_f^\theta - 0.0296\log\left(a_{Fe^{2+}}^3\right) + 0.0296\log\left(a_{H^+}^8\right)$$

$$U_f = U_f^\theta - 0.0887\log[Fe^{2+}] - 0.2366\ \text{pH}$$

$$U_f = 1.5124 - 0.2366\ \text{pH}$$

Reaction (g), $Fe_2O_3 + 6H^+ + 2e^- \leftrightarrow 2Fe^{2+} + 3H_2O$

$$U_g = U_g^\theta - \frac{RT}{2F}\ln\frac{\left(a_{Fe^{2+}}^2\right)\left(a_{H_2O}^3\right)}{\left(a_{H^+}^6\right)}$$

$$U_g = 0.728 - 0.592\log[10^{-6}] - 0.1775\ \text{pH}$$

$$U_g = 1.083 - 0.1775\ \text{pH}$$

Reaction (h) is a chemical equilibrium, $2Fe^{3+} + 3H_2O \leftrightarrow Fe_2O_3 + 6H^+$

$$K_{sp} = \frac{\left(a_{Fe^{3+}}^2\right)\left(a_{H_2O}^3\right)}{\left(a_{H^+}^6\right)} \approx \frac{\left(a_{Fe^{3+}}^2\right)}{\left(a_{H^+}^6\right)} = e^{\frac{nFU^\theta}{RT}}$$

.

$a_{H_2O} = 1$, n=2 From, equilibrium data U^θ=-0.043 V (reactions d and g)

$$2\ln(a_{Fe^{2+}}) - 6\ln(a_{H^+}) = \frac{2FU^\theta}{RT}$$

$$pH = \frac{FU^\theta}{(2.303)3RT} - \frac{1}{3}\log[10^{-6}] = 1.76$$

Reaction (i), $3Fe_2O_3 + 2H^+ + 2e^- \leftrightarrow 2Fe_3O_4 + H_2O$

$$U_i = U_i^\theta - \frac{RT}{nF}\ln\frac{1}{\left(a_{H^+}^2\right)}$$

$$U_i = 0.221 - 0.0592\ \text{pH}$$

Reaction (j), $Fe_3O_4 + H_2O + OH^- + 2e^- \leftrightarrow 3HFeO_2^-$

add this reaction to $$H_2O \leftrightarrow H^+ + OH^-$$

which results in a form of the same equation in terms of the proton activity

$$Fe_3O_4 + 2H_2O + 2e^- \leftrightarrow 3HFeO_2^- + H^+$$

$$U_j = U_j^\theta - \frac{RT}{nF}\ln\frac{\left(a_{HFeO_2^-}^3\right)}{\left(a_{H^+}\right)}$$

$$U_i = -1.819 - 0.0887\log[10^{-6}] - 0.0295\ \text{pH}$$

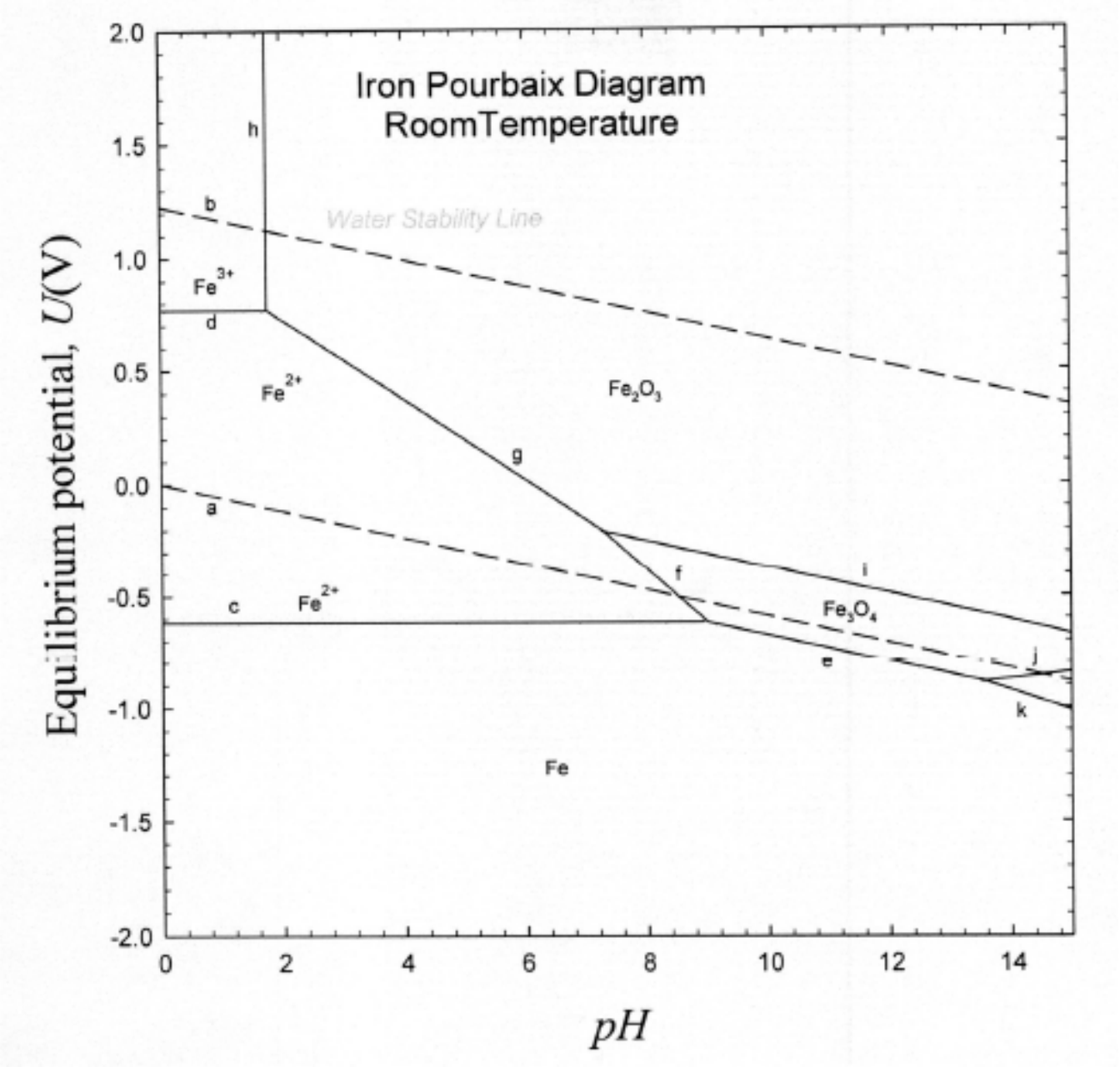
$$U_i = -1.2869 - 0.0295\ \text{pH}$$

Reaction (k), $HFeO_2^- + 3H^+ + 2e^- \leftrightarrow Fe + 2H_2O$

$$U_k = U_k^\theta - \frac{RT}{nF}\ln\frac{1}{\left(a_{HFeO_2^-}\right)\left(a_{H^+}^3\right)}$$

$$U_i = 0.493 + 0.0295\log[10^{-6}] - 0.0886\ \text{pH}$$

$$U_i = 0.316 - 0.0886\ \text{pH}$$


Iron Pourbaix Diagram
RoomTemperature
Water Stability Line
Equilibrium potential, U(V)
pH
h
b
d
a
c
g
f
i
j
k
e
Fe3+
Fe2+
Fe2+
Fe2O3
Fe3O4
Fe
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0
2
4
6
8
10
12
14

Use the information in Appendix A to determine the dissociation constant for water, K_w.

$$H_2O \leftrightarrow H^+ + OH^-$$

Use entries 4 and 9 from Appendix A

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \qquad U^\theta = 0.401 \text{ V}$$
$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \qquad U^\theta = 1.229 \text{ V}$$

$$\frac{nFU^\theta}{RT} = \ln \frac{(a_{H^+})(a_{OH^-})}{a_{H2O}}$$

$$K_w = \frac{(a_{H^+})(a_{OH^-})}{a_{H2O}} \approx (a_{H^+})(a_{OH^-}) = e^{\frac{nFU^\theta}{RT}} = e^{\frac{F(0.401-1.229)}{RT}} = \boxed{10^{-14}}$$

Determine the solubility product K_{sp} for $PbSO_4$.

The desired equilibrium is

$$PbSO_4 \leftrightarrow Pb^{2+} + SO_4^{2-}$$

We can write this a the sum of two electrochemical equations

$$PbSO_4 + 2e^- \leftrightarrow Pb + SO_4^{2-} \qquad U^{\theta}\text{=-0.356 V}$$
$$Pb \leftrightarrow Pb^{2+} + 2e^- \qquad U^{\theta}\text{=-0.126 V}$$

$$K = e^{\frac{nFU^{\theta}}{RT}} = e^{\frac{2F(-0.356+0.126)}{RT}} = \boxed{1.67 \times 10^{-8}}$$

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PROBLEM 2-21

U1 = 0.153 [V] *oxidation of Cu*

U2 = 0.521 [V] *oxidation of Cu+*

$$K = \exp\left[F \cdot \left(\frac{U1 - U2}{R \cdot T}\right)\right]$$

R = 8.314 [J/mol-K]

T = 298.15 [K]

F = 96485 [Coulomb/mol]

SOLUTION

Unit Settings: SI C kPa kJ mass deg

F = 96485 [Coulomb/mol] K = 6.014E-07 R = 8.314 [J/mol-K]

T = 298.2 [K] U1 = 0.153 [V] U2 = 0.521 [V]

No unit problems were detected.

$Cu^{2+} + e^- \rightarrow Cu^+$ $U_1^\theta = 0.153$ V

$Cu^+ + e^- \rightarrow Cu$ $U_2^\theta = 0.521$ V

Subtract to get

$Cu + Cu^{2+} \rightleftharpoons 2\,Cu^+$ $U^\theta = U_1^\theta - U_2^\theta$

$K = \exp\frac{F}{RT}(U_1^\theta - U_2^\theta) = 6 \times 10^{-7}$

at 298 K

Explain what a liquid junction is and why the potential of cells with liquid junctions cannot be determined from thermodynamics alone.

In many electrochemical cells, the two electrodes are exposed to solutions of different composition. Since an ionic path must exist between the two electrodes, diffusion of ions from across the region of non-uniform composition can occur even in the absence of current flow. A small potential difference is associated with this liquid junction. Thermodynamics analysis, however, assumes that the system is in equilibrium, which is not valid when transport across this liquid junction is present. To account for small correction in potential associated with this liquid junction, transport must be treated.

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PROBLEM 2-22

$c = 100$ [mol/m^3] *concentration of lithium salt*

$\rho = 1286$ [kg/m^3] *density of electrolyte*

basis of 1 m3 of electrolyte

$$m = \frac{c}{\rho - c \cdot MW}$$

$MW = 0.1519$ [kg/mol]

Calculate Debye length

$R = 8.314$ [J/mol-K]

$T = 303.15$ [K]

$F = 96485$ [coulomb/mol]

$dc = 64$

$p = 8.85419 \times 10^{-12}$ [coulomb/(V-m)]

$\varepsilon = dc \cdot p$

$sum = 2 \cdot c$

$$\lambda = \sqrt{\varepsilon \cdot R \cdot \frac{T}{F \cdot F \cdot sum}}$$

convert molality to ionic strength, 1:1 electrolyte, no change

ACTIVITY COEFFICIENT

solvent constants

$e = 1.6 \times 10^{-19}$ [coulomb]

$\rho_s = 1205$ [kg/m^3]

$$\alpha = \sqrt{\rho_s} \cdot \frac{F \cdot F \cdot e \cdot \sqrt{2}}{8 \cdot \pi \cdot [\varepsilon \cdot R \cdot T]^{1.5}}$$

$I = m$

$Ba = 1$ [(kg/mol)$^{0.5}$]

$$\ln[\gamma] = \frac{-\alpha \cdot \sqrt{I}}{1 + Ba \cdot \sqrt{I}}$$

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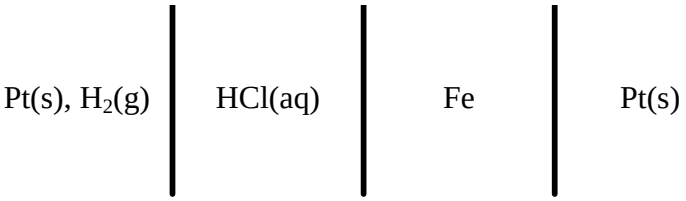
SOLUTION

Unit Settings: SI C kPa kJ mass deg

α = 1.705 [$(kg/mol)^{0.5}$]
Ba = 1 [$(kg/mol)^{0.5}$]
c = 100 [mol/m^3]
dc = 64
e = 1.600E-19 [coulomb]
ε = 5.667E-10 [Coulomb/(V-m)]
F = 96485 [coulomb/mol]
γ = 0.6884
I = 0.07869 [mol/kg]
λ = 8.758E-10 [m]
m = 0.07869 [mol/kg]
MW = 0.1519 [kg/mol]
p = 8.854E-12 [coulomb/(V-m)]
R = 8.314 [J/mol-K]
ρ = 1286 [kg/m^3]
ρ_s = 1205 [kg/m^3]
sum = 200 [mol/m^3]
T = 303.2 [K]

No unit problems were detected.

Consider the electrochemical cell below. Iron corrodes to form Fe^{2+}. Develop an expression for *U*, and determine the value of the standard potential.



At the negative electrode

$$Fe^{2+} + 2e^- \leftrightarrow Fe \qquad (-0.440\ V)$$

Positive

$$2H^+ + 2e^- \leftrightarrow H_2 \qquad (0.0\ V)$$

The overall reaction is

$$2H^+ + Fe \leftrightarrow H_2 + Fe^{2+} \quad n=2,\ U^{\theta}=-0.44\ V$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{nF}\ln\prod a_i{}^{s_i}, \tag{2-11}$$

$$U = U^{\theta}_{\text{cell}} - \frac{RT}{2F}\ln\frac{a_{H2}a_{Fe2+}}{a^2_{H+}},$$

$$U = 0.440 - \frac{RT}{2F}\ln\left({p_{H2}}/{p^o}\right) - \frac{RT}{2F}\ln\frac{a_{Fe2+}}{a^2_{H+}},$$

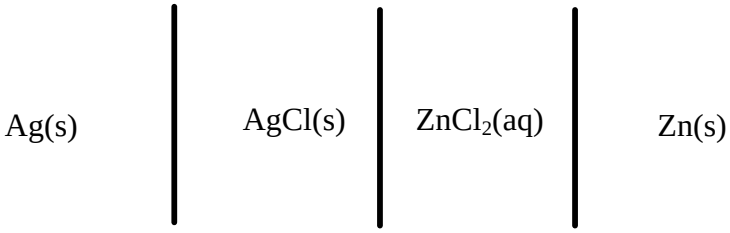
This is not the desired form, we'd like to have this expression is terms of common, measurable activity coefficients: $m_{FeCl_2}\gamma_{FeCl_2}$.

HCl $a_{HCl} = (a_{H^+})(a_{Cl^-})$ $\qquad a_{FeCl_2} = (a_{Fe^{2+}})(a^2_{Cl^-})$

$$\frac{a_{Fe2+}}{a^2_{H+}} = \frac{a_{FeCl_2}}{a^2_{HCl}} = \frac{4\left(\gamma_{\mp}^{FeCl_2}m_{FeCl_2}\right)^3}{1\left(\gamma_{\mp}^{HCl}m_{HCl}\right)^4}$$

$$U = 0.440 - \frac{RT}{2F}\ln\left({p_{H2}}/{p^o}\right) - \frac{RT}{F}\ln(2) - \frac{3}{2}\frac{RT}{F}\left(\ln\gamma_{\mp}^{FeCl_2}m_{FeCl_2}\right) + \frac{2RT}{F}\left(\gamma_{\mp}^{HCl}m_{HCl}\right)$$

Find the expression for the equilibrium potential of the cell at 25 °C.



At the negative electrode

$$Zn^{2+} + 2e^- \leftrightarrow Zn \qquad (-0.763\ V)$$

Positive

$$AgCl + e^- \leftrightarrow Ag + Cl^- \qquad (0.222\ V)$$

The overall reaction is

$$2AgCl + Zn \leftrightarrow 2Ag + Zn^{2+} + 2Cl^-$$

$$U^{\theta}{}_{\text{cell}} = U_+^{\theta} - U_-^{\theta} = 0.222 + 0.763 = 0.985\ \text{V}$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{nF}\ln\prod a_i{}^{s_i}, \qquad (2\text{-}11)$$

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{2F}\ln a_{ZnCl_2} = U_{\text{cell}}^{\theta} - \frac{RT}{2F}\ln 4\left(\gamma_{\mp}^{ZnCl_2} m_{ZnCl_2}\right)^3$$

$$\boxed{U = 0.985 - \frac{RT}{F}\ln(2) - \frac{3}{2}\frac{RT}{F}\ln m\gamma_{\mp}}$$

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"!PROBLEM 2-25"

I1=0.1
i2=0.3
Ba1=0.9992
Ba2=1.588

ln(gamma_nacl)=(-1.1762*1*sqrt(I1))/(1+Ba1*sqrt(I1))
ln(gamma_Cacl2)=(-1.1762*2*sqrt(I2))/(1+Ba2*sqrt(I2))

SOLUTION

Unit Settings: SI C kPa kJ mass deg

Ba1 = 0.9992 Ba2 = 1.588
γ_{Cacl2} = 0.502 γ_{nacl} = 0.7538
I1 = 0.1 i2 = 0.3

No unit problems were detected.

Parametric Table: Table 1

	I	γ_{nacl}	γ_{Cacl2}
Run 1	0.0001	0.9884	0.977
Run 2	0.003129	0.9396	0.8828
Run 3	0.006159	0.918	0.8427
Run 4	0.009188	0.9022	0.814
Run 5	0.01222	0.8895	0.7912
Run 6	0.01525	0.8787	0.7722
Run 7	0.01828	0.8693	0.7557
Run 8	0.02131	0.8609	0.7411
Run 9	0.02433	0.8532	0.728
Run 10	0.02736	0.8462	0.7161
Run 11	0.03039	0.8398	0.7052
Run 12	0.03342	0.8338	0.6951
Run 13	0.03645	0.8281	0.6858
Run 14	0.03948	0.8228	0.6771
Run 15	0.04251	0.8178	0.6689
Run 16	0.04554	0.8131	0.6612
Run 17	0.04857	0.8086	0.6539
Run 18	0.0516	0.8043	0.6469
Run 19	0.05463	0.8002	0.6404
Run 20	0.05766	0.7963	0.6341
Run 21	0.06069	0.7925	0.6281
Run 22	0.06372	0.7889	0.6224
Run 23	0.06674	0.7854	0.6169
Run 24	0.06977	0.7821	0.6116
Run 25	0.0728	0.7788	0.6066
Run 26	0.07583	0.7757	0.6017
Run 27	0.07886	0.7726	0.597
Run 28	0.08189	0.7697	0.5924
Run 29	0.08492	0.7669	0.5881
Run 30	0.08795	0.7641	0.5838
Run 31	0.09098	0.7614	0.5797
Run 32	0.09401	0.7588	0.5757
Run 33	0.09704	0.7562	0.5719
Run 34	0.1001	0.7537	0.5681

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Parametric Table: Table 1

	I	γ_{nacl}	γ_{Cacl2}
Run 35	0.1031	0.7513	0.5645
Run 36	0.1061	0.749	0.5609
Run 37	0.1092	0.7467	0.5575
Run 38	0.1122	0.7444	0.5541
Run 39	0.1152	0.7422	0.5509
Run 40	0.1182	0.7401	0.5477
Run 41	0.1213	0.738	0.5446
Run 42	0.1243	0.7359	0.5416
Run 43	0.1273	0.7339	0.5386
Run 44	0.1304	0.7319	0.5357
Run 45	0.1334	0.73	0.5329
Run 46	0.1364	0.7281	0.5301
Run 47	0.1394	0.7262	0.5274
Run 48	0.1425	0.7244	0.5248
Run 49	0.1455	0.7226	0.5222
Run 50	0.1485	0.7209	0.5197
Run 51	0.1516	0.7192	0.5172
Run 52	0.1546	0.7175	0.5148
Run 53	0.1576	0.7158	0.5124
Run 54	0.1607	0.7142	0.5101
Run 55	0.1637	0.7126	0.5078
Run 56	0.1667	0.711	0.5055
Run 57	0.1697	0.7094	0.5033
Run 58	0.1728	0.7079	0.5011
Run 59	0.1758	0.7064	0.499
Run 60	0.1788	0.7049	0.4969
Run 61	0.1819	0.7035	0.4949
Run 62	0.1849	0.702	0.4929
Run 63	0.1879	0.7006	0.4909
Run 64	0.1909	0.6992	0.4889
Run 65	0.194	0.6979	0.487
Run 66	0.197	0.6965	0.4851
Run 67	0.2	0.6952	0.4833
Run 68	0.2031	0.6939	0.4815
Run 69	0.2061	0.6926	0.4797
Run 70	0.2091	0.6913	0.4779
Run 71	0.2122	0.69	0.4762
Run 72	0.2152	0.6888	0.4744
Run 73	0.2182	0.6876	0.4728
Run 74	0.2212	0.6864	0.4711
Run 75	0.2243	0.6852	0.4694
Run 76	0.2273	0.684	0.4678
Run 77	0.2303	0.6828	0.4662
Run 78	0.2334	0.6817	0.4647
Run 79	0.2364	0.6805	0.4631
Run 80	0.2394	0.6794	0.4616
Run 81	0.2424	0.6783	0.4601
Run 82	0.2455	0.6772	0.4586
Run 83	0.2485	0.6761	0.4571
Run 84	0.2515	0.675	0.4557
Run 85	0.2546	0.674	0.4543
Run 86	0.2576	0.6729	0.4529

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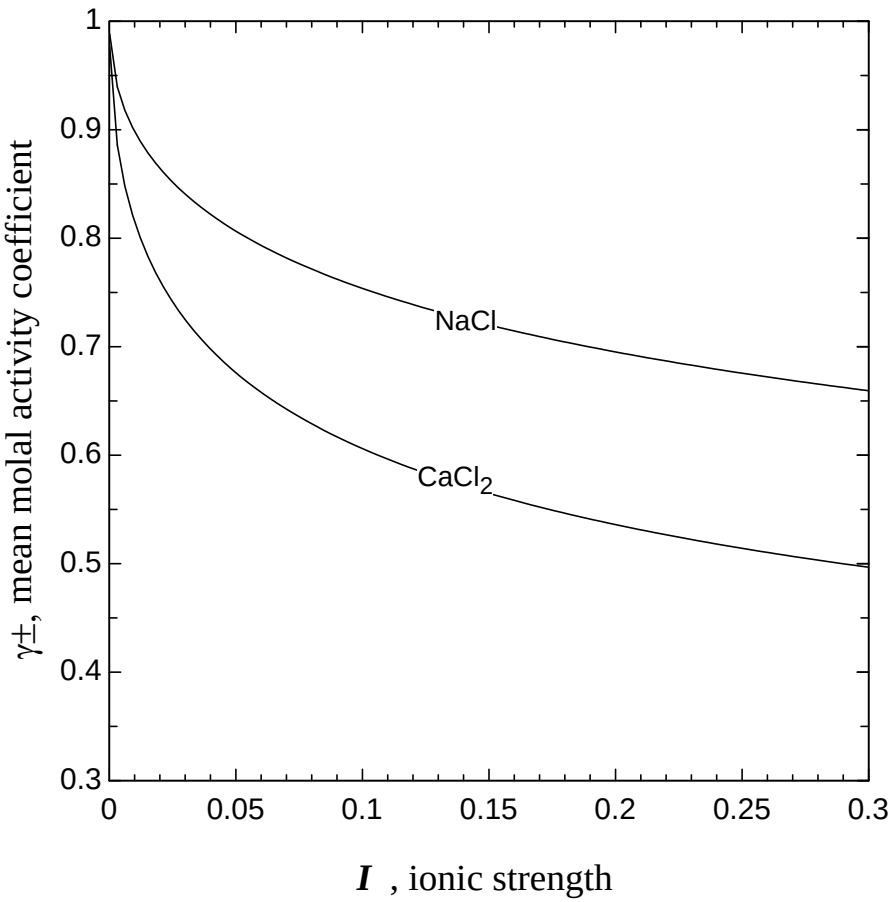
Parametric Table: Table 1

	I	γ_{nacl}	γ_{Cacl2}
Run 87	0.2606	0.6719	0.4515
Run 88	0.2636	0.6709	0.4501
Run 89	0.2667	0.6699	0.4487
Run 90	0.2697	0.6689	0.4474
Run 91	0.2727	0.6679	0.4461
Run 92	0.2758	0.6669	0.4448
Run 93	0.2788	0.6659	0.4435
Run 94	0.2818	0.665	0.4422
Run 95	0.2849	0.664	0.4409
Run 96	0.2879	0.6631	0.4397
Run 97	0.2909	0.6622	0.4385
Run 98	0.2939	0.6613	0.4373
Run 99	0.297	0.6603	0.4361
Run 100	0.3	0.6594	0.4349



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PROBLEM 2-26

$I = 0.3$ [mol/kg] *ionic strength of 0.1 m MgCl2*

$R = 8.314$ [J/mol-K]

$T = 298.15$ [K]

$F = 96485$ [coulomb/mol]

$dc = 80.4$ *dielectric constant for water at 25 C*

$p = 8.85419 \times 10^{-12}$ [coulomb/(V-m)]

$\varepsilon = dc \cdot p$

ACTIVITY COEFFICIENT

solvent constants

$e = 1.602 \times 10^{-19}$ [coulomb]

$\rho_s = 997.1$ [kg/m^3] *density of water*

$$\alpha = \sqrt{\rho_s} \cdot \frac{F \cdot F \cdot e \cdot \sqrt{2}}{8 \cdot \pi \cdot [\varepsilon \cdot R \cdot T]^{1.5}}$$

$$B = F \cdot \frac{\sqrt{\rho_s}}{\sqrt{\varepsilon \cdot R \cdot \frac{T}{2}}}$$

$a1 = 8.0 \times 10^{-10}$ [m]

$a2 = 3.0 \times 10^{-10}$ [m]

$a = 0.5 \cdot [a1 + a2]$

$$\ln[\gamma] = \frac{-2 \cdot \alpha \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

a = 5.500E-10 [m]
a1 = 8.000E-10 [m]
a2 = 3.000E-10 [m]
α = 1.13 [(kg/mol)$^{0.5}$]
B = 3.244E+09 [(kg/mol)$^{0.5}$/m]
dc = 80.4
e = 1.602E-19 [coulomb]
ε = 7.119E-10 [Coulomb/(V-m)]

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F = 96485 [coulomb/mol]
γ = 0.5345
I = 0.3 [mol/kg]
p = 8.854E-12 [coulomb/(V-m)]
R = 8.314 [J/mol-K]
ρ_s = 997.1 [kg/m^3]
T = 298.2 [K]

No unit problems were detected.

Parametric Table: experimental data

	I [mol/kg]	x [(mol/kg)$^{0.5}$]	γ	$gamm_{lim}$	γ_{exp}
Run 1	*0.001*	*0.03162*	*0.9661*	*0.9649*	*0.965*
Run 2	*0.005*	*0.07071*	*0.9287*	*0.9232*	*0.927*
Run 3	*0.01*	*0.1*	*0.9035*	*0.8931*	*0.902*
Run 4	*0.05*	*0.2236*	*0.8174*	*0.7766*	*0.821*
Run 5	*0.1*	*0.3162*	*0.7687*	*0.6994*	*0.778*
Run 6	*1*	*1*	*0.5889*	*0.3229*	*0.657*

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PROBLEM 2-27

I=0.1 [mol/kg]

ionic strength of NaCl, equivalent to molality

$R = 8.314$ [J/mol-K]

$T = 298.15$ [K]

$F = 96485$ [coulomb/mol]

$dc = 80.4$ *dielectric constant for water at 25 C*

$p = 8.85419 \times 10^{-12}$ [coulomb/(V-m)]

$\varepsilon = dc \cdot p$

ACTIVITY COEFFICIENT

solvent constants

$e = 1.602 \times 10^{-19}$ [coulomb]

$\rho_s = 997.1$ [kg/m^3] *density of water*

$$\alpha = \sqrt{\rho_s} \cdot \frac{F \cdot F \cdot e \cdot \sqrt{2}}{8 \cdot \pi \cdot [\varepsilon \cdot R \cdot T]^{1.5}}$$

$$B = F \cdot \frac{\sqrt{\rho_s}}{\sqrt{\varepsilon \cdot R \cdot \frac{T}{2}}}$$

$a1 = 4.0 \times 10^{-10}$ [m]

$a2 = 3.0 \times 10^{-10}$ [m]

$a = 0.5 \cdot [a1 + a2]$

$$\mathbf{ln}[\gamma] = \frac{-\alpha \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}}$$

$gamm_{lim} = \mathbf{exp}[-\alpha \cdot \sqrt{I}]$

$x = \sqrt{I}$

$gamma_{exp}$=1

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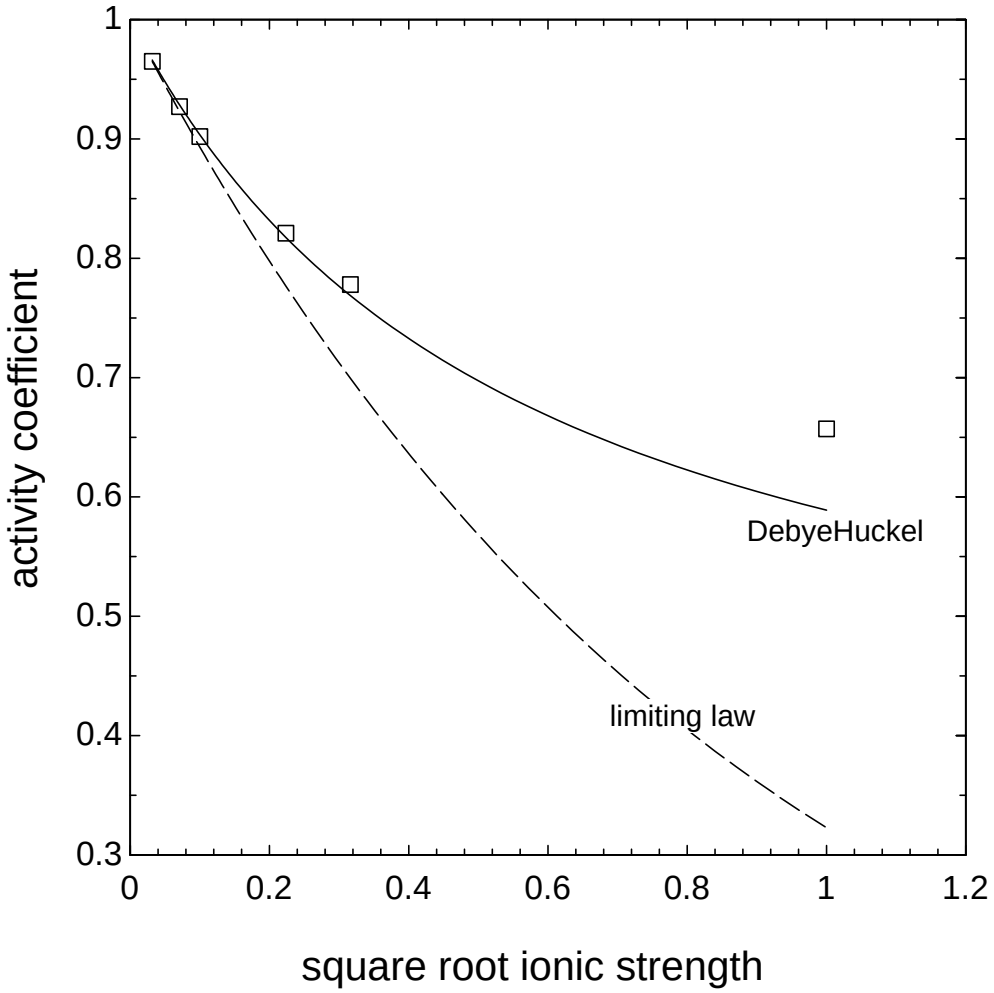
Parametric Table: experimental data

	I [mol/kg]	x [(mol/kg)$^{0.5}$]	γ	$gamm_{lim}$	γ_{exp}
Run 1	0.001	0.03162	0.9661	0.9649	0.965
Run 2	0.005	0.07071	0.9287	0.9232	0.927
Run 3	0.01	0.1	0.9035	0.8931	0.902
Run 4	0.05	0.2236	0.8174	0.7766	0.821
Run 5	0.1	0.3162	0.7687	0.6994	0.778
Run 6	1	1	0.5889	0.3229	0.657



Before concerns about mercury became widespread, the calomel electrode was commonly used. Crystals of KCl are added to produce a saturated solution. What advantage does a saturated solution provide? The saturated calomel electrode has an equilibrium potential of 0.242 V, which is lower than the standard potential of 0.2676. Can this 25 mV difference be determined from thermodynamics? Why or why not? The solubility of KCl in water at 25 °C is 360 g KCl/100 g water.

Because the dissolved KCl can diffuse slowly out of the reference electrode, adding crystals keeps the solution saturated. This helps to maintain stable performance longer. The 25 mV offset cannot be determined from thermodynamics alone. The cell has a liquid junction. Transport is required to analyze the potential difference. Chloride and potassium ions will diffuse from high to low concentration. Unless you just happen to be measuring the potential in a solution of exactly the same concentration, ions will be moving and the concentration profile will affect the measured potential.

A solid oxide fuel cell operates at 1000 °C. The overall reaction is

$$0.5O_2 + H_2 \leftrightarrow H_2O$$

a. Calculate the standard potential at 25 °C assuming that reactants and products are gases.
b. Calculate the standard potential at 1000 °C using equation 2-18.
c. Using the correlation for heat capacity as a function of temperature shown below, calculate the standard potential at 1000 °C. Comment on the assumption used in part (b) that $\Delta S°$ is constant.

$$C_p = A + BT + CT^{-2}$$

	A [J/mol-K]	10^3B [J/mol-K^2]	$10^{-5}C$ [J-K/mol]
H_2O	30.54	10.29	0
O_2	29.96	4.184	-16.7
H_2	27.28	3.26	0.50

(a) The overall reaction is

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$$

Using the data from Appendix C

$$\Delta G_{Rx} = \Delta G^o_{f,H_2O} = -228{,}572 \text{ J}$$

$$U^\theta = \frac{-\Delta G_{Rx}}{nF} = \frac{228{,}572}{(2)96485} = \boxed{1.184 \text{ V}}$$

(b) Appendix C has data for 25 °C

$$S_{H_2} = 130.5 \frac{\text{J}}{\text{mol K}}$$

$$S_{H_2} = 205.3 \frac{\text{J}}{\text{mol K}}$$

$$S_{H_2O} = 188.7 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{Rx} = 188.7 - 130.5 - \frac{205.3}{2} = -44.45 \frac{\text{J}}{\text{mol} - \text{K}}$$

$$U(1000) = 1.184 + (1000 - 25)\left({}^{-44.45}/_{(2)96485}\right) = \boxed{0.959 \text{ V}}$$

(c)

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p$$

$$\Delta H(T) - \Delta H(T_o) = \int \Delta C_p dT$$

$$\Delta A = 30.54 - \frac{1}{2}(29.96) - 27.28 = -11.72$$

$$1000\Delta B = 10.29 - \frac{1}{2}(4.184) - 3.26 = 4.938$$

$$10^{-5}\Delta C = 0 - \frac{1}{2}(-16.7) - 0.5 =$$

$$\Delta H(T) = \Delta H(T_o) + \int_{T_o}^{T} \left(\Delta A + \Delta B T + \frac{\Delta C}{T^2}\right) dT$$

$$\Delta H(T) = \Delta H(T_o) + \Delta A(T - T_o) + \frac{\Delta B(T^2 - T_o^2)}{2} - \Delta C\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

$$\left(\frac{\partial\left({}^{U}/_{T}\right)}{\partial T}\right)_p = \frac{\Delta H(T)}{nFT^2}$$

$$n\left(\frac{U}{T} - \frac{U^\theta}{T_o}\right) = \int_{T_o}^{T} \frac{\Delta H(T)}{T^2} + \frac{\Delta A(T - T_o)}{T^2} + \frac{\Delta B(T^2 - T_o^2)}{2T^2} - \Delta C\left(\frac{1}{T^3} - \frac{1}{T^2 T_o}\right) dT$$

$$U = \left(\frac{T}{T_o}\right) U^\theta + \frac{T}{2F}\left[\Delta H^o\left(\frac{1}{T} - \frac{1}{T_o}\right) + \Delta A\left(\ln\frac{T}{T_o} + \frac{T}{T_o} - 1\right) + \frac{(T - T_o)^2}{2T}\left(\Delta B + \frac{\Delta C}{T T_o^2}\right)\right]$$

at 1000 °C, *U*=0.9219 V. This is compared to the value calculated assuming that Δ*S* is constant, U=0.959 V. There is almost a 40 mV difference.

Alloys of LiSn are possible electrodes for batteries. There are many phases possible, but we want to focus on the reaction

$$3\text{LiSn} + 4\text{Li}^+ + 4\text{e}^- = \text{Li}_7\text{Sn}_3$$

The standard potential of this reaction at 25 °C is 0.530 V (vs. reference Li electrode). If the enthalpy of the reaction

$$3\text{LiSn} + 4\text{Li} = \text{Li}_7\text{Sn}_3$$

is -226kJ/mol Li_7Sn_3, estimate the standard potential at 400 °C.

Assuming ΔH is constant

$$U = U_o \frac{T}{T_o} + \frac{\Delta H}{nF}\left(\frac{T}{T_o} - 1\right)$$

$$U = 0.530\frac{673}{298} + \frac{-226{,}000}{4F}\left(\frac{673}{298} - 1\right) = 0.460 \text{ V}$$

Find the equilibrium constant, K_{eq}, for Pt dissolution reaction at 25 °C.

$$PtO + 2H^+ = Pt^{2+} + H_2O$$

The following thermodynamic data are provided, $\Delta G_f^{Pt^{2+}} = 229.248 \frac{kJ}{mol}$, and

$$PtO + 2H^+ + 2e^- = Pt + H_2O \qquad U^\theta = 0.980 \text{ V}$$

Find the Gibbs energy of formation for PtO

$$PtO + 2H^+ + 2e^- = Pt + H_2O \qquad U^\theta = 0.980 \text{ V}$$

$$H_2 = 2H^+ + 2e^- \qquad U^\theta = 0.0 \text{ V}$$

sum to get

$$PtO + H_2 = Pt + H_2O \qquad U^\theta = 0.980 \text{ V}$$

$$\Delta G_{Rx} = \Delta G^o_{f,H2O} - \Delta G^o_{f,PtO} = -nFU^\theta = 2F(0.980)$$

$$\Delta G^o_{PtO} = -48{,}014 \text{ J mol}^{-1}$$

dissolution reaction of interest is

$$PtO + 2H^+ = Pt^{2+} + H_2O$$

$$\Delta G_{Rx} = \Delta G^o_{f,Pt2+} + \Delta G^o_{f,H2O} - \Delta G^o_{f,PtO} = 40{,}133 \text{ J mol}^{-1}$$

$$K_{sp} = e^{-\Delta G_{Rx}/RT} = 9.2 \times 10^{-8} = \frac{a_{Pt2+}}{a^2_{H+}}$$

a. Write the overall reaction and determine the standard potential for the lead-acid battery.

b. Develop an expression for the equilibrium potential, *U*, for the lead acid battery as a function of electrolyte composition. The final expression should include the molality and activity coefficient.

c. The potentials of the two electrodes relative to a Hg-Hg_2SO_4 reference electrode at 25 °C has been measured. What is the likely reaction at the reference electrode? If the standard Gibbs energy of formation of Hg_2SO_4 is -625.8 kJ/mol and the standard Gibbs energy of formation of $SO_4^{2-}$is -744.62 kJ/mol, determine the standard potential of the positive (lead oxide electrode) relative to the reference electrode. How does this value compare to the measured value of 0.96 V? Explain the possible cause of any difference.

d. Given that the potential difference between the positive electrode and the reference electrode is 1.14 V, estimate the activity coefficient for sulfuric acid ($\gamma_{\pm}$) at 6 m. For this evaluation, you may assume that the activity of water is one.

e. Does the potential of the lead electrode (Pb) relative to the reference electrode depend on the molality of the sulfuric acid? Explain your answer.

a. The cell can be written as

α	β	γ	δ	ε	α′
Pb(s)	PbO_2(s)	$PbSO_4$(s)	H_2SO_4(aq)	$PbSO_4$(s)	Pb(s)

At the negative electrode

$$PbSO_4 + 2e^- \leftrightarrow Pb + SO_4^{2-} \qquad (-0.356\ V)$$

and the positive electrode

$$PbO_2 + SO_4^{2-} + 4H^+ + 4e^- \leftrightarrow PbSO_4 + 2H_2O \qquad (1.685\ V)$$

The overall reaction is

$$Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \leftrightarrow 2PbSO_4 + 2H_2O$$

$$U_{\text{cell}}^{\theta} = U_{+}^{\theta} - U_{-}^{\theta} = 1.685 - (-0.356) = 2.041\ \text{V}$$

b) $$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{nF}\ln\prod a_i{}^{s_i} \qquad (2\text{-}11)$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{2F}\ln\frac{a_{\text{H2O}}^2 a_{\text{PbSO4}}^2}{a_{\text{H2SO4}}^2 a_{\text{Pb}} a_{\text{PbO2}}}$$

the activity of solids is one

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{2F}\ln\frac{a_{\text{H2O}}^2}{a_{\text{H2SO4}}^2}$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{F}\ln a_{\text{H2O}} + \frac{RT}{F}\ln a_+^{\nu_+} a_-^{\nu_-}$$

$a_+ = m_+\gamma_+$ $a_- = m_-\gamma_-$

$m_+ = \nu_+ m$ $m_- = \nu_- m$

$$a_+^{\nu+} a_-^{\nu-} = \nu_+^{\nu+} m^{\nu+} \nu_-^{\nu-} m^{\nu-} \gamma_+^{\nu+} \gamma_-^{\nu-}$$

$\gamma_\pm^{\nu} \equiv \gamma_+^{\nu+}\gamma_-^{\nu-}$ $\nu \equiv \nu^+ + \nu^-$

$a_+^{\nu+} a_-^{\nu-} = m^{\nu}\nu_+^{\nu+}\nu_-^{\nu-}\gamma_\pm^{\nu}$

for H_2SO_4, $\nu^+ = 2$ $\nu^- = 1$ $\nu = 3$

$$a_+^2 a_-^1 = m^3(2)^2(1)^1\gamma_\pm^3$$

$$U = U^{\theta}{}_{\text{cell}} - \frac{RT}{F}\ln a_{\text{H2O}} + \frac{RT}{F}\ln 4m^3\gamma_\pm^3$$

$$\boxed{U = U^{\theta}{}_{\text{cell}} - \frac{RT}{F}\ln a_{\text{H2O}} + \frac{RT}{F}\ln 4 + \frac{3RT}{F}\ln m\gamma_\pm}$$

c) and the positive electrode

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \leftrightarrow PbSO_4 + 2H_2O \qquad (1.685\ \text{V})$$

reference or negative electrode

$$Hg_2SO_4 + 2e^- \leftrightarrow 2Hg + SO_4^{2-} \qquad (?)$$

Use thermodynamic data from Appendix C to find the standard potential for the reference electrode

$$\Delta G_{Rx} = \Delta G^o_{f,SO_4^{2-}} - \Delta G^o_{f,HgSO_4}$$

$$\Delta G_{Rx} = -744.62 - (-625.8) = -118.8\ \text{kJ mol}^{-1}$$

$$U_-^{\theta} = \frac{-\Delta G_{Rx}}{nF} = \frac{118{,}800}{(2)96485} = 0.6157\ \text{V}$$

$$\boxed{U_{\text{cell}}^{\theta} = U_+^{\theta} - U_-^{\theta} = 1.685 - 0.6157 = 1.069\ \text{V}}$$

The measured value at 1 m H_2SO_4, 0.96 V, difference is about 100 mV. Likely because the activity coefficient of the sulfuric acid and that of water are not one.

d) The overall reaction is

$$2Hg + PbO_2 + 2H_2SO_4 + 4H^+ \leftrightarrow Hg_2SO_4 + PbSO_4 + 2H_2O$$

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{2F}\ln\frac{a^2_{H2O}a_{Hg2SO4}a_{PbSO4}}{a^2_{H2SO4}a_{Hg}a_{PbO2}}$$

$$U = U^\theta{}_{\text{cell}} - \frac{RT}{F}\ln a_{H2O} + \frac{RT}{2F}\ln a^2_{H2SO4}$$

$$U = U^\theta \quad - \frac{RT}{F}\ln a_{H2O} + \frac{RT}{F}\ln 4 + \frac{R3T}{F}\ln m\gamma_\pm$$

At 6 m, $U_{PbO2} = 1.07$ V and $U_{Hg/Hg2SO4} = -0.07$ V

$$U = 1.07 - (-0.07) = 1.14 \text{ V}$$

assume the activity coefficient of water is one

$$1.14 \text{ V} = 1.069 + 0.036 + 0.0771 \ln m\gamma_\pm$$

$$\boxed{\gamma_\pm = 0.262}$$

e)

$$PbSO_4 + 2e^- \leftrightarrow Pb + SO_4^{2-}$$
$$Hg_2SO_4 + 2e^- \leftrightarrow 2Hg + SO_4^{2-}$$

$$Pb + Hg_2SO_4 \leftrightarrow 2Hg + PbSO_4$$

Although the sulfate ion appears in the reactions, it does not appear in the overall reaction. Therefore, *U* does not depend on the molality of the acid.

Rework Illustration 2-7 (reference electrode example) with a Ag_2SO_4 reference electrode rather than a Hg_2SO_4 reference electrode. The standard potential for this reference electrode reaction (below) is 0.654V.

$$U_{ref}^{\theta} = 0.654$$

$$\mathrm{Ag_2SO_4 + 2e^- = 2Ag + SO_4^{2-}}$$

Unchanged from Illustration 2.7 $U_{O2/SHE} = 1.252$ $U_{Cu/SHE} = 0.3192$

$$U_{\mathrm{Ag_2SO_4}/SHE} = U_{ref}^{\theta} - \frac{RT}{nF}\ln\left(\frac{c_{\mathrm{SO_4^{2-}}}}{1M}\right)$$

assuming that the sulfate concentration is 1.8 M

$$U_{\mathrm{Ag_2SO_4}/SHE} = 0.654 - \frac{RT}{2F}\ln(1.8) = 0.6588\ \mathrm{V}$$

$$U_{O2/ref} = U_{O2/SHE} - U_{ref/SHE} = 1.252 - 0.6588 = 0.5931\ \mathrm{V}$$

$$U_{Cu/ref} = U_{Cu/SHE} - U_{ref} = 0.3192 - 0.6588 = -0.3396\ \mathrm{V}$$

$$U_{O2/Cu} = U_{O2/ref} - U_{\frac{Cu}{ref}} = 0.5931 + 0.3396 = 0.933\ \mathrm{V}$$

As expected the value of the cell didn't change, each electrode was at a slightly different potential relative to the different reference electrode.

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Problem 3-1

MW = 0.32924 [kg/mol]

T = 298.15 [K]

R = 8.314 [J/mol-K]

F = 96485 [coulomb/mol]

m = 0.00001 [kg]

V = 0.0001 [m^3]

$$c_K = 3 \cdot \frac{m}{MW \cdot V}$$

$c_{ferri} = c_{ferro}$

$$c_{ferro} = 0.5 \cdot \frac{m}{MW \cdot V}$$

U = 0.26 [V] *because potential is at std potential, the concentration of ferri and ferro are the same*

SOLUTION

Unit Settings: SI C kPa kJ mass deg

c_{ferri} = 0.1519 [mol/m^3]
c_K = 0.9112 [mol/m^3]
m = 0.00001 [kg]
R = 8.314 [J/mol-K]
U = 0.26 [V]

c_{ferro} = 0.1519 [mol/m^3]
F = 96485 [coulomb/mol]
MW = 0.3292 [kg/mol]
T = 298.2 [K]
V = 0.0001 [m^3]

No unit problems were detected.

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Problem 3-1b&c

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

$F = 96485$ [coulomb/mol]

$MW = 0.32924$ [kg/mol]

$m = 0.00001$ [kg]

$V = 0.0001$ [m^3]

$$c_K = 3 \cdot \frac{m}{MW \cdot V}$$

$$c_{ferri} = c_{ferro}$$

$$c_{ferro} = 0.5 \cdot \frac{m}{MW \cdot V}$$

$$I = c_K + c_{ferri} + c_{ferro}$$

$$\lambda = \sqrt{\varepsilon \cdot \varepsilon_r \cdot R \cdot \frac{T}{F \cdot F \cdot I}}$$

$\varepsilon = 8.854 \times 10^{-12}$ [$m^{-3} \cdot kg^{-1} \cdot s^4 \cdot A^2$]

$\varepsilon_r = 78$

Part c

increase the ionic strength, neglect ferri and ferro cyanide concentrations

$c = 100$ [mol/m^3]

$I_n = 2 \cdot c$

$$\lambda_n = \sqrt{\varepsilon \cdot \varepsilon_r \cdot R \cdot \frac{T}{F \cdot F \cdot I_n}}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$c = 100$ [mol/m^3]
$c_{ferri} = 0.1519$ [mol/m^3]
$c_{ferro} = 0.1519$ [mol/m^3]
$c_K = 0.9112$ [mol/m^3]
$\varepsilon = 8.854E-12$ [$m^{-3} \cdot kg^{-1} \cdot s^4 \cdot A^2$]
$\varepsilon_r = 78$
$F = 96485$ [coulomb/mol]
$I = 1.215$ [mol/m^3]

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I_n = 200 [mol/m^3]
λ = 1.230E-08 [m]
λ_n = 9.586E-10 [m]
m = 0.00001 [kg]
MW = 0.3292 [kg/mol]
R = 8.314 [J/mol-K]
T = 298 [K]
V = 0.0001 [m^3]

No unit problems were detected.

Repeat Illustration 3-2(a) for the situation where the potential (0.10V) is relative to a Ag/AgCl reference electrode. The equilibrium potential for the saturated Ag/AgCl electrode is 0.197 V. Please comment on any differences that you observe between the two solutions.

From Illustration 3-2, $3966\ \text{A m}^{-2}$

The equilibrium potentials are as follows

$U^{\theta}_{SCE} = 0.2576\ \text{V}$	saturated	$U_{SCE} = 0.242\ \text{V}$
$U^{\theta}_{\text{Ag/AgCl}} = 0.222\ \text{V}$	saturated	$U_{\text{Ag/AgCl}} = 0.197\ \text{V}$

For the ferri-ferro cyanide reaction, U=0.3674 V, see illustration 3-2.

The overpotential is therefore

$$\eta_s = 0.1 + 0.197 - 0.3674 = -0.074\ \text{V}$$

Using the Butler-Volmer equation

$$i = i_o\left[\exp\left(\frac{(1-\beta)F\eta_s}{RT}\right) - \exp\left(-\frac{\beta F\eta_s}{RT}\right)\right]. \tag{3-16}$$

$$i = i_o\left[\exp\left(\frac{F\eta_s}{2RT}\right) - \exp\left(-\frac{F\eta_s}{RT}\right)\right].$$

solving for the current density

using an area of 0.75 cm^2

$$\boxed{\begin{aligned} i &= -14{,}602\ \text{A m}^{-2} \\ I &= -1.095\ \text{A} \end{aligned}}$$

Because the potential of the AgCl reference electrode is smaller than that of the SCE, the absolute value for the overpotential at 0.1 V is higher, resulting in a larger cathodic current.

Hydrogen gassing can be a serious problem for lead-acid batteries. Consider two reactions on the negative electrode: the desired reaction for charging

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \qquad U^{\theta}\text{=-0.356 V}$$

and an undesired side reaction

$$2H^+ + 2e^- \rightarrow H_2 \qquad U^{\theta}\text{=0.0 V}$$

a) The exchange-current densities for the two reactions are $i_{o,PbSO_4} = 100\ \text{Am}^{-2}$, and $i_{o,H_2} = 6.6 \times 10^{-10}\ \text{Am}^{-2}$, where the exchange current density for the hydrogen reaction is on pure lead. Calculate the current density for each reaction if the electrode is held at a potential of -0.44 V relative to a hydrogen reference electrode. The temperature is 25 °C, and the transfer coefficients are 0.5.

b) With Sb impurity in the lead, the exchange current density of the hydrogen reaction increases to $3.7\text{x}10^{-4}$ A m^{-2}. Repeat the calculation of part (a) in the presence of antimony. Assuming that all impurities cannot be eliminated, what implications do these results have for the operation of the battery?

a)

$$\eta_s^{Pb} = -0.44 - (-0.356) = -0.084\ \text{V}$$

$$\eta_s^{H2} = -0.44 - (0.0) = -0.44\ \text{V}$$

Using the Butler-Volmer equation

$$i = i_o \left[\exp\left(\frac{\alpha_a F \eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_s}{RT}\right)\right], \tag{3-17}$$

Solving for the current density

$$i_{Pb} = -493\ \text{A m}^{-2}$$

$$i_{H2} = -3.5 \times 10^{-6}\ \text{A m}^{-2}$$

b) Use the provided exchange current density for the case of hydrogen evolution in the presence of impurities,

$$i_{H2} = -1.9\ \text{A m}^{-2}$$

There is a large increase in current density. The increase is not so large as to affect the energy efficiency—less than one percent of the current is going to hydrogen formation. On the other hand, this generated hydrogen must be managed; that is vented or recombined with oxygen to prevent a build-up of hydrogen in the cell.

Data for the exchange current density for oxygen evolution on a lead oxide surface are provided as a function of temperature. Develop an expression for i_o as a function of temperature. What is the activation energy? If the transfer coefficient is a constant at 0.5 and the overpotential is 0.7 V, at what temperature will the current density for oxygen reduction be 5 Am^{-2}?

T, °C	i_o, A m^{-2}
15	6.9×10^{-7}
25	1.7×10^{-6}
35	7.6×10^{-6}
45	1.35×10^{-5}

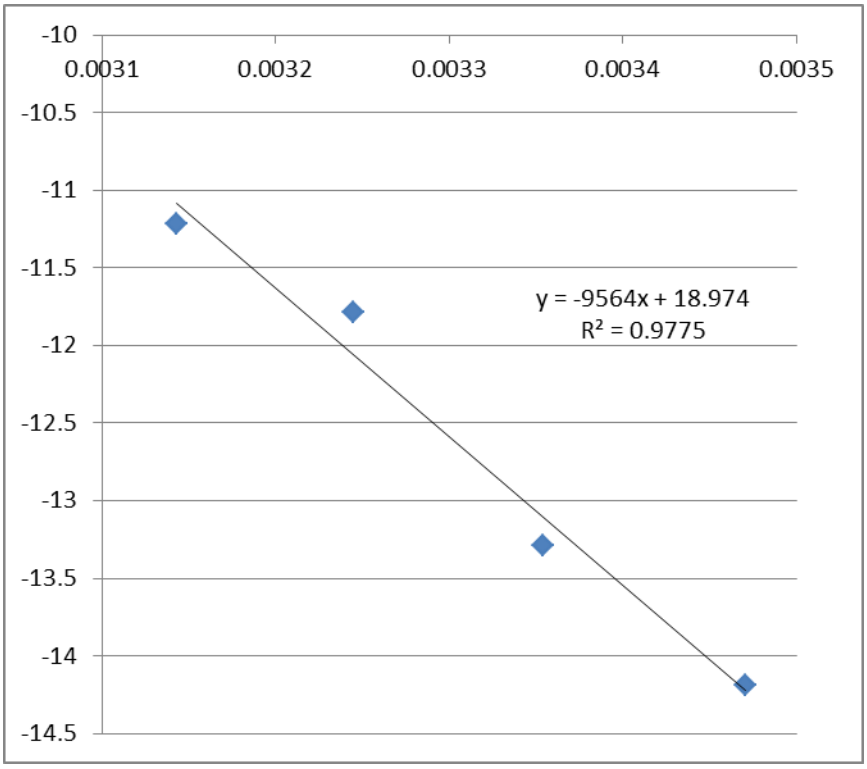
Assume a form for the dependence on temperature

$$i_o(T) = A\exp\left\{\frac{-E_a}{RT}\right\}. \tag{3-18}$$

or

$$\ln i_o = \ln A - \frac{-E_a}{RT}.$$

The tabulated data are plotted as shown the figure: the logarithm of exchange current density versus reciprocal of temperature, and the data fitted with a line.



$$\ln i_o(T) = \frac{-9564}{T} + 18.974$$

$$\frac{E_a}{R} = 9564 \text{ K}$$

$$E_a = R(9564 \text{ K}) = 79.5 \text{ kJ mol}^{-1}$$

α_a=0.5 η_s=0.7 V

$$i = i_o(T)\exp\left\{\frac{\alpha_a}{RT}\eta_s\right\} = 5 \text{ A m}^{-2}$$

Solve for T,

$$\boxed{T = 317 \text{ K} = 44 \text{ °C}}$$

The following reaction is an outer-sphere reaction that occurs in KOH.

$$[MnO_4]^- + e^- \leftrightarrow [MnO_4]^{2-} \quad (1)$$

Would you expect the reaction to have a larger or small reorganizational energy compared to an isotope exchange reaction for manganese? What does this imply about the reaction rate?

$$Mn^{2+} + Mn^{*3+} \leftrightarrow Mn^{3+} + Mn^{*2+} \quad (2)$$

Just as in the iron (II)/iron (III) example from the text, it is expected that the reorganizational energy would be smaller for the larger permanganate ions. We would expect that the rate for this first reaction to be faster than the isotope exchange reaction.

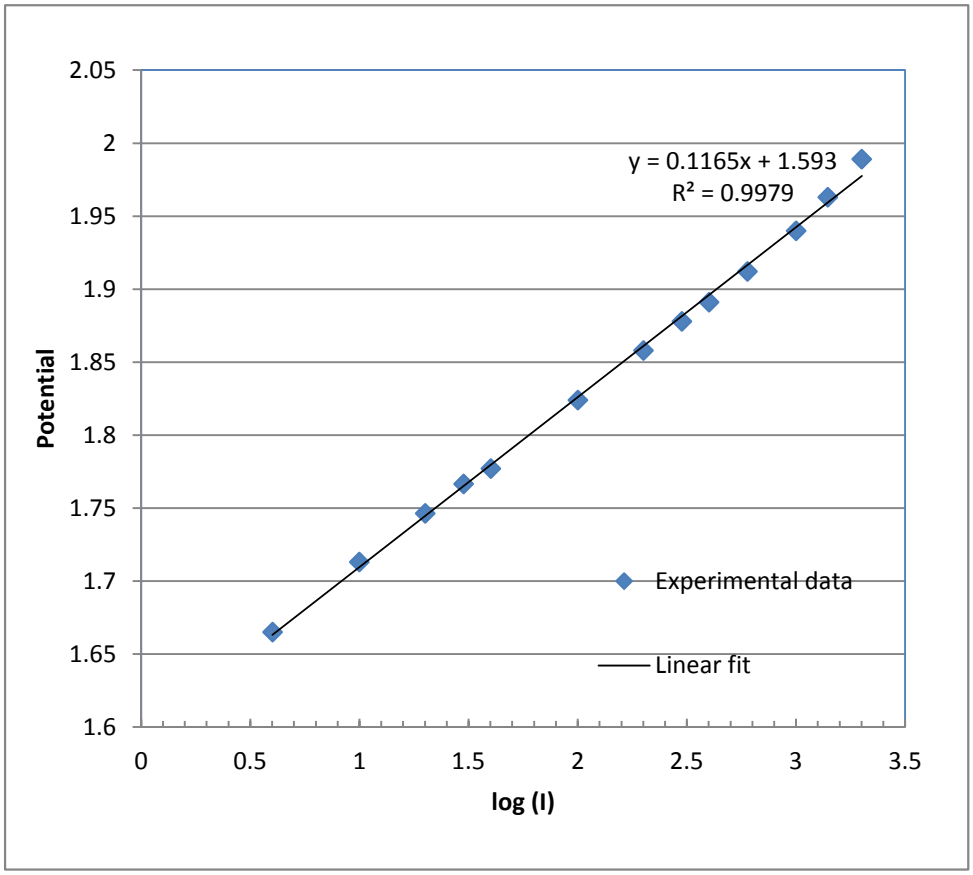
Reactions with Mn(II) are challenging experimentally because of disproportionation,

$$2Mn^{3+} \leftrightarrow Mn^{2+} + Mn^{4+}$$

Nonetheless, the rate constant for the first reaction is orders of magnitude larger than for the isotope exchange. A. G. Sykes, *Advances in Inorganic Chemistry and Radiochemistry*, **10**, 153-245 (1968).

I, Am-2	log (I)	Potential, V
4	0.60206	1.665
10	1	1.713
20	1.30103	1.7465
30	1.477121	1.7665
40	1.60206	1.777
100	2	1.824
200	2.30103	1.858
300	2.477121	1.878
400	2.60206	1.891
600	2.778151	1.912
1000	3	1.94
1400	3.146128	1.963
2000	3.30103	1.989

From fit: Tafel slope is 0.12 V/decade
To get the exchange current density one would need to know how the potential is referenced



The evolution of oxygen is an important process in the lead-acid battery. Assume that the positive electrode of the flooded lead-acid battery is at its standard potential (entry 2 in Appendix A), calculate the overpotential for the oxygen evolution reaction. It is reported that the Tafel slope for this reaction is 120 mV/decade at 15 °C. What is the transfer coefficient, α_a? If the exchange current density is 6.9×10^{-7} A·m^{-2}, what is the current density for oxygen evolution? You may neglect the small change in equilibrium potential with temperature.

The Tafel slope is

$$\ln 10 \frac{RT}{\alpha_a F} = 0.12 \text{ V}$$

$$\alpha_a = \frac{\ln 10}{0.12} \frac{RT}{F} = 0.48$$

$$\eta_s = 1.685 - 1.229 = 0.456 \text{ V}$$

$$i = i_o e^{\frac{\alpha_a F}{RT} \eta_s}$$

$$i_o = 6.9 \times 10^{-7} \text{A m}^{-2}$$

$$i = 4.4 \text{ mA m}^{-2}$$

i

The tabulated data are for the dissolution of zinc in a concentrated alkaline solution. These data are measured using a Hg/HgO reference electrode. Under the conditions of the experiment, the equilibrium potential for the zinc electrode is -1.345 V relative to the HgO electrode.

Potential, V	i, A m^{-2}
-1.335	58
-1.325	150
-1.315	300
-1.305	600
-1.295	1100
-1.285	1970
-1.275	3560
-1.265	6300
-1.255	11,500
-1.245	20,000
-1.235	36,800
-1.225	66,000

a. Please determine the exchange current density and Tafel slope that best represent these data.

b. For the same electrolyte, the potential of a SCE electrode is 0.2 V more positive than the Hg/HgO reference. If the potential of the zinc is held at -1.43 V relative to the SCE electrode, what is the current density for the oxidation of zinc?

a)

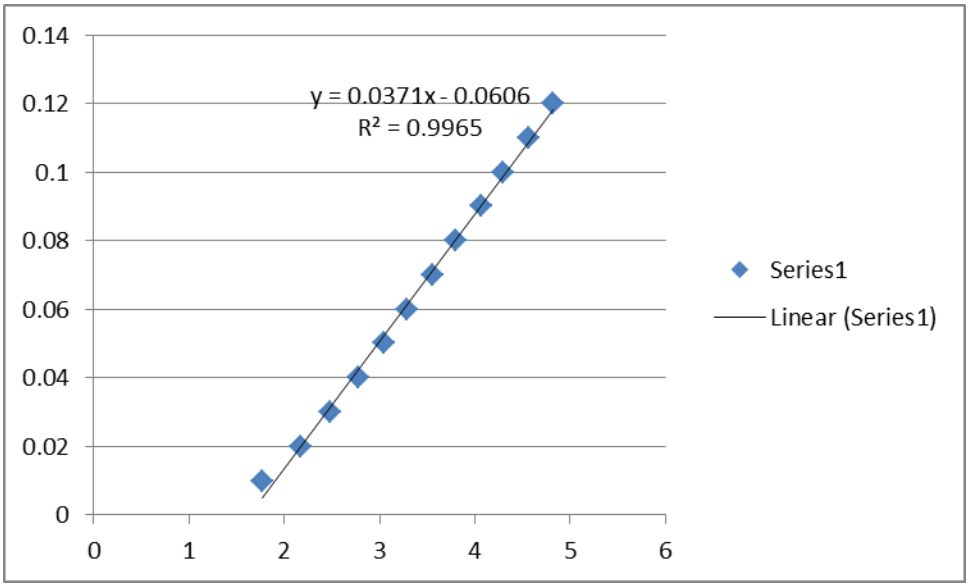
$$\eta_s = V - U$$

The data provide V, subtract (U=-1.345) to get the overpotential. Then create a Tafel plot, fit line through data

$$\eta_s = 0.037 \log i - 0.0606$$

The Tafel slope is

37 mV per decade



Find current density where the overpotential is zero,

$$\eta_s = 0.037 \log i - 0.0606 = 0$$

$$\log i_o = \frac{0.0606}{0.037}$$

$$i_o = 43.4 \text{ A m}^{-2}$$

b) V=-1.43 V (relative to SCE)

$$V_{HgO} = V_{SCE} - 0.2$$

$$\eta_s = -1.43 + 0.2 + 1.345 = 0.115 \text{ V}$$

$$i = 55.7 \text{ kA m}^{-2}$$

Derive Equation 3-28. For a reaction at 80 °C, and with (α_a+α_c)=2, at what value for the overpotential will the error with the Tafel equation be less than 1 percent?

$$\text{error} = \frac{\text{Tafel} - BV}{BV} = \frac{T}{BV} - 1 = E$$

$$1 + E = \frac{T}{BV}$$

$$1 + E = \frac{i_o e^{\frac{\alpha_a F}{RT}\eta_s}}{i_o \left\{ e^{\frac{\alpha_a F}{RT}\eta_s} - e^{\frac{-\alpha_c F}{RT}\eta_s} \right\}}$$

$$\frac{1}{1+E} = 1 - e^{\frac{-(\alpha_c+\alpha_a)F}{RT}\eta_s}$$

$$\frac{E}{1+E} = e^{\frac{-(\alpha_c+\alpha_a)F}{RT}\eta_s}$$

$$|\eta_s| = \frac{RT}{F}\frac{1}{(\alpha_c+\alpha_a)}\ln\frac{E}{1+E}$$

E=0.01, *T*=298 K

$$|\eta_s| = \frac{B}{298}\frac{T}{(\alpha_c+\alpha_a)} = \frac{RT}{F}\frac{1}{(\alpha_c+\alpha_a)}\ln\frac{E}{1+E}$$

$$B = \frac{298R}{F}\frac{1}{(\alpha_c+\alpha_a)}\ln\frac{E}{1+E} = 0.119\ \text{V}$$

b) at 80 °C, $\alpha_c + \alpha_a = 2$

$$|\eta_s| = \frac{RT}{F}\frac{1}{(\alpha_c+\alpha_a)}\ln\frac{E}{1+E} = 0.070\ \text{V}$$

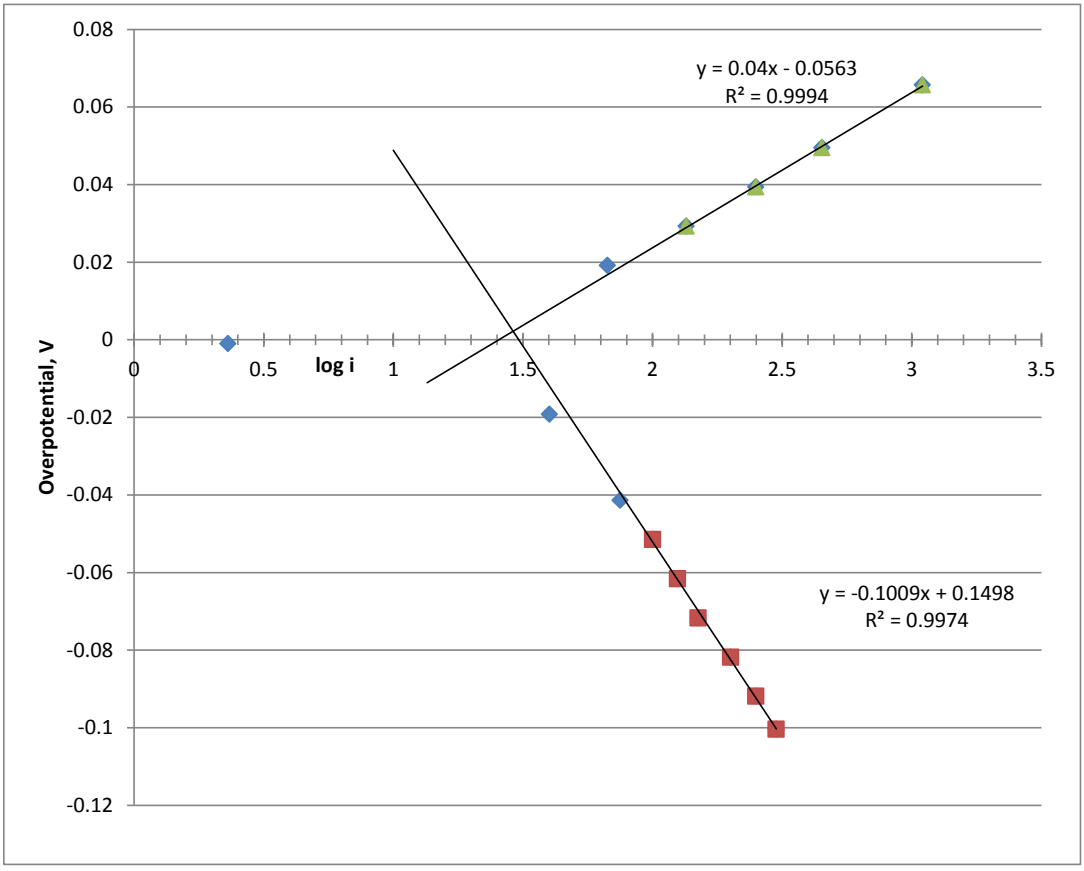
Problem 3-10

In order to model the deposition of copper, the following data have been collected for 1 M $CuSO_4$ in 1 M H_2SO_4. The temperature is 25 °C, and a copper plated reference electrode was used. From these data determine the parameters for the Butler-Volmer kinetic expression. The reaction is

$$Cu \rightarrow Cu^{2+} + 2e^{-}, \qquad U^{\theta}=0.337 \text{ V}$$

I, A/m^2	η_s, V	I, A/m^2	η_s, V
-300	-0.1004	-40	-0.0192
-250	-0.0919	-2.3	-0.00101
-200	-0.0818	67	0.0192
-150	-0.0717	135	0.0293
-125	-0.0616	250	0.0394
-100	-0.0515	450	0.0495
-75	-0.0414	1100	0.0657

Option 1. Plot high and low overpotential on Tafel plot

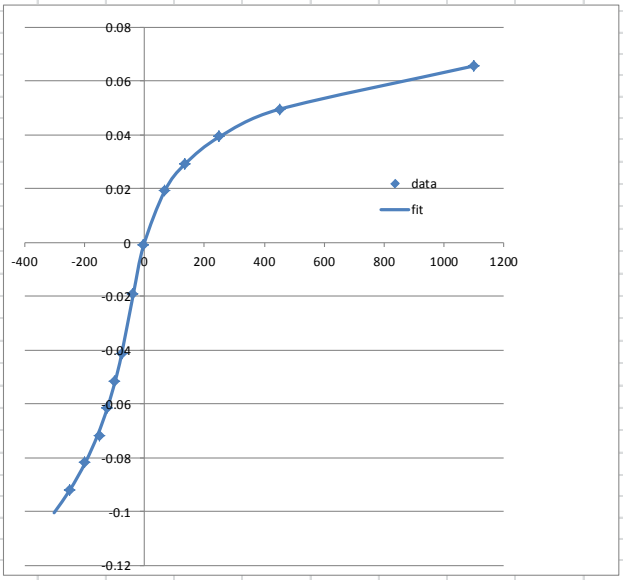


Point where the lines cross, i_o=10^(1.45)=28 A/m^2
Slopes of line are 2.303RT/(Fα)

Problem 3-10

Option 2. One can fit the entire range with the full Butler Volmer equation.

		F/RT	38.92378		
	0.59	c	0.582902		
	29	i	30.87821		
	1.48	a	1.399753		
overpotential	Current density	logi	calculated current		error
-0.1004	-300	2.477121	-301.138		-1.13817
-0.0919	-250	2.39794	-248.22		1.780223
-0.0818	-200	2.30103	-197.192		2.808487
-0.0717	-150	2.176091	-156.471		-6.47135
-0.0616	-125	2.09691	-123.844		1.156157
-0.0515	-100	2	-97.4707		2.529339
-0.0414	-75	1.875061	-75.7572		-0.75715
-0.0192	-40	1.60206	-36.8876		3.112352
-0.00101	-2.3	0.361728	-2.36904		-0.06904
0.0192	67	1.826075	67.92062		0.920617
0.0293	135	2.130334	136.5036		1.503575
0.0394	250	2.39794	251.5699		1.569928
0.0495	450	2.653213	448.013		-1.987
0.0657	1100	3.041393	1100.289		0.289034
					81.83432



	Option 1	Option 2
α_c	0.59	0.58
α_a	1.48	1.40
Io	28	30.9 A/m^2

In section 3.7, equation 3-33 was developed using Tafel kinetics, illustrating the effect of mass transfer on the current density. Derive the equivalent expression for linear kinetics. Explain the difference in shape of graphs for *i vs.* η_s between linear and Tafel kinetics.

For linear kinetics

$$i = i_o(\alpha_c + \alpha_a)\frac{F}{RT}\eta_s$$

at steady state

$$nFk_c(c_b - c_s) = i_o(\alpha_c + \alpha_a)\frac{F}{RT}\eta_s$$

$$nFk_c(c_b - c_s) = i_{o,ref}\frac{c_s}{c_b}(\alpha_c + \alpha_a)\frac{F}{RT}\eta_s = i$$

$$(c_b - c_s) = \frac{i}{nFk_c} \qquad c_s = \frac{i}{i_{o,ref}}c_b\frac{RT}{(\alpha_c+\alpha_a)\eta_s F}$$

$$c_b\left\{1 - \frac{i}{i_{o,ref}}\frac{RT}{(\alpha_c + \alpha_a)\eta_s F}\right\} = \frac{i}{nFk_c}$$

$$i\left\{\frac{1}{nFk_c c_b} + \frac{RT}{i_{o,ref}(\alpha_c + \alpha_a)\eta_s F}\right\} = 1$$

$$i = \frac{1}{\frac{1}{nFk_c c_b} + \frac{RT}{i_{o,ref}(\alpha_c + \alpha_a)\,F\eta_s/RT}}$$

$$i_{lim} = nFk_c c_b$$

$$\frac{i}{i_{lim}} = \frac{1}{1 + \frac{i_{lim}}{i_o(\alpha_c + \alpha_a)\,F\eta_s/RT}}$$

Metal is deposited via a two-electron reaction with current voltage data as shown at the right. The equilibrium potential is -0.5 V vs. the same reference electrode used to measure the data. The bulk concentration is 100 mol/m^3. You may assume that the exchange current density is linearly dependent on the concentration of the reactant (*i.e.*, you may use Eq. 3-33). Assume 25 °C.

a. Is mass transfer important? If so, please determine a value for the mass-transfer coefficient.

b. Assuming Tafel kinetics, find the values of α_c and i_o. Comment on the applicability of this assumption. Can the normal Tafel fitting procedure be used for this part? Why or why not?

c. If the mass-transfer coefficient were reduced by a factor of 2 (cut in half), please predict the current that would correspond to an applied potential of -0.9V.

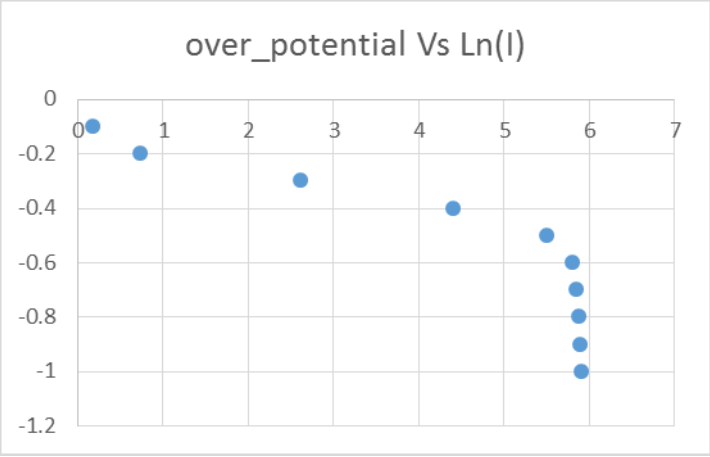
Additional Hints: You need to consider carefully which points you use in fitting the kinetic parameters. Also, it is a good idea to normalize the error when fitting the current.

a) Inspection of the data clearly shows the current plateauing at about 360 A m^{-2}. This feature is an indication of mass-transfer limitations.

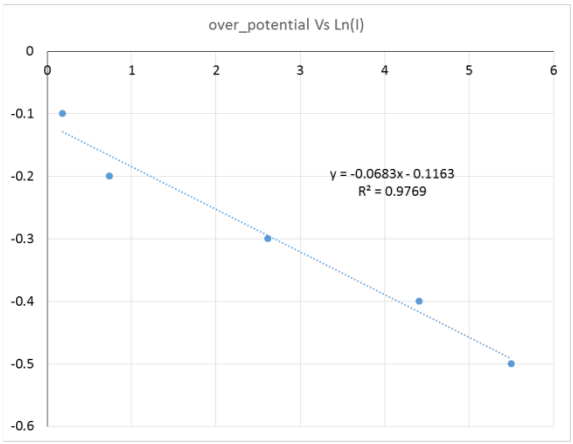
$$i_{lim} = nFk_c c_b$$

$$k_c = \frac{i_{lim}}{nFc_b} = \frac{360}{(2)(96485)(100)} = 1.87 \times 10^{-5}\ \text{m s}^{-1}$$

b) The kinetic parameters can be obtained from a Tafel plot,



We clearly see from the Semi log Tafel plot of all of the data that the line we get is not straight, thus the Tafel slope cannot be used since the points are out of Tafel region. However we may smartly choose the first few data points in the kinetic region and use those to fit to a line to get the Tafel slope, as in graph. Then this slope can be used to find the BV parameters and by doing so we get the following values



$$\eta_s = -0.1163 - 0.068 \ln i$$

$0.0683 = \frac{RT}{\alpha_c F}$ $\alpha_c = 0.378$

at i=1, $\eta_s = -0.1163$ $i_o = e^{\frac{-\alpha_c F}{RT}\eta_s}$

$$i_o = 0.077 \text{ A m}^{-2}$$

c) $i_{lim} = \frac{360}{2} = 180 \text{ A m}^{-2}$

$V_{app} = -0.9 \text{ V}$ $\eta_s = -0.4 \text{ V}$

$$\frac{1}{i} = \frac{1}{i_{lim}} + \frac{1}{i_o e^{\frac{-\alpha_c F}{RT}\eta_s}}$$

Solve for the current density

$$i = -24 \text{ A m}^{-2}$$

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Chapter 3 problem 13, create polarization curve for hydrogen oxygen fuel cell

$I = 10000$ [A/m^2] *set current density*

for polarization curve, comment out line above and use table

$U_c = 1.229$ [V]

ANODE POLARIZATION

linear kinetics

$i_{oa} = 14000$ [A/m^2]

$$I = i_{oa} \cdot 2 \cdot \frac{F}{R \cdot T} \cdot -\phi_{2a}$$

$$\eta_a = -\phi_{2a}$$

OHMIC POLARIZATION

$L = 0.00004$ [m]

$\kappa = 10$ [1/Ω-m]

$$R_{ohm} = \frac{L}{\kappa}$$

$$\eta_{ohm} = I \cdot R_{ohm}$$

$$\phi_{2c} = \phi_{2a} - \eta_{ohm}$$

CATHODE POLARIZATION

$i_{oc} = 9.0 \times 10^{-7}$ [A/m^2]

$$I = i_{oc} \cdot \mathbf{exp}\left[-a_c \cdot \frac{F}{R \cdot T} \cdot \left(\phi_{1c} - \phi_{2c} - U_c\right)\right]$$

$a_c = 1$

$F = 96485$ [Coulomb/mol]

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

$$\eta_c = \phi_{1c} - \phi_{2c} - U_c$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$a_c = 1$

$\eta_c = -0.594$ [V]

$\eta_a = 0.009171$ [V]

$\eta_{ohm} = 0.04$ [V]

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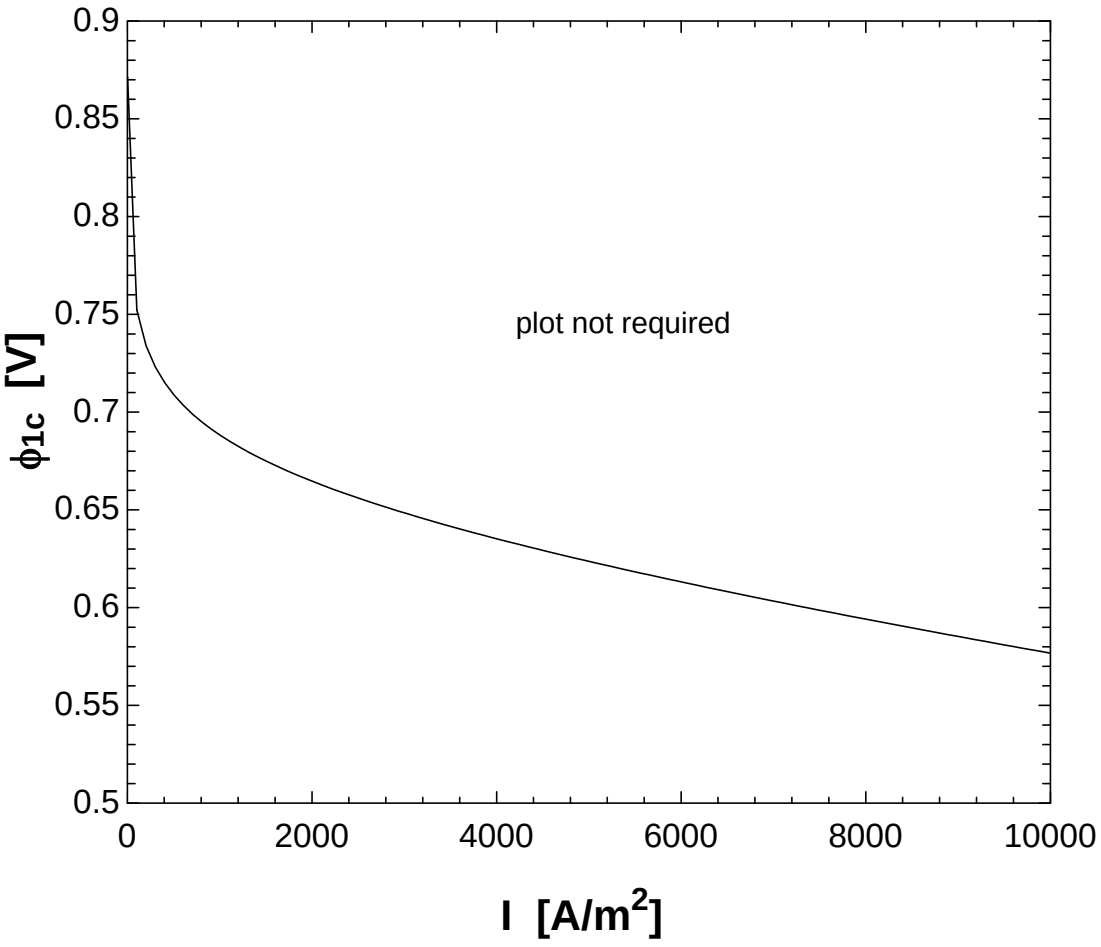
F = 96485 [Coulomb/mol]
i_{oa} = 14000 [A/m^2]
κ = 10 [1/Ω-m]
ϕ_{1c} = 0.5859 [V]
ϕ_{2c} = -0.04917 [V]
R_{ohm} = 0.000004 [Ω-m^2]
Uc = 1.229 [V]

I = 10000 [A/m^2]
i_{oc} = 9.000E-07 [A/m^2]
L = 0.00004 [m]
ϕ_{2a} = -0.009171 [V]
R = 8.314 [J/mol-K]
T = 298 [K]

No unit problems were detected.



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PROBLEM 3-14

Full cell Zn/Ni battery

part B and C

I=-821 [A/m^2];

current density of cell

phi$_{2m}$=2.0 [V]

$\phi_{m1} = 0$ [V] *potential of zinc metal arbitrarily set to zero*

Butler Volmer Kinetics for Zn reaction

$I = Rf1 \cdot i_{1o} \cdot [\exp(eta1 \cdot frt \cdot aa1) - \exp(-eta1 \cdot frt \cdot ac1)]$

$Rf1 = 2$ *roughness factor for Zn electrode*

$i_{1o} = 60$ [A/m^2] *exchange current density for Zn*

$eta1 = \phi_{m1} - \phi_{21} - U1$

$U1 = 0$ [V]

$F = 96485$ [Coulomb/mol]

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

$$frt = \frac{F}{R \cdot T}$$

$aa1 = 1.5$

$ac1 = 0.5$

Ohm's law for separator

$L = 0.002$ [m] *thickness of separator*

$\kappa = 60$ [1/Ω-m] *conductivity of electrolyte*

$$\phi_{22} = \phi_{21} - L \cdot \frac{I}{\kappa}$$

Butler-Volmer equation for Ni Reaction

reduction, therefore current is negative

$-I = Rf2 \cdot i_{2o} \cdot [\exp(eta2 \cdot frt \cdot aa2) - \exp(-eta2 \cdot frt \cdot ac2)]$

$Rf2 = 100$ *roughness factor for Ni electrode*

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$i_{2o} = 0.61$ [A/m^2] *exchange current density for Ni*

$eta2 = \phi_{2m} - \phi_{22} - U2$

$U2 = 1.74$ [V]

$aa2 = 0.5$

$ac2 = 0.5$

$p1 = \phi_{21} - \phi_{22}$

$p2 = p1 + eta1$

$p3 = p2 - eta2$

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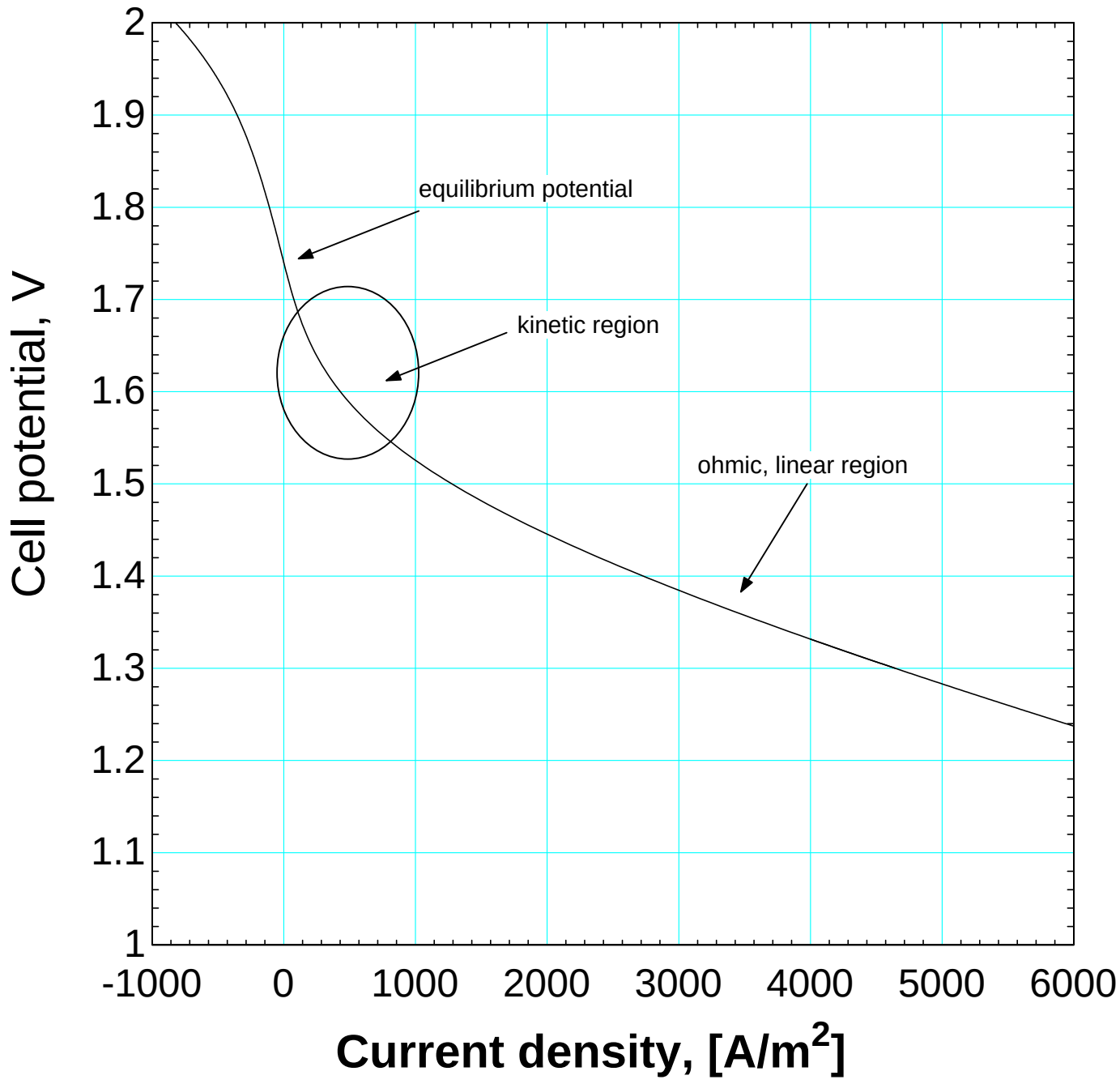


Problem 3-15

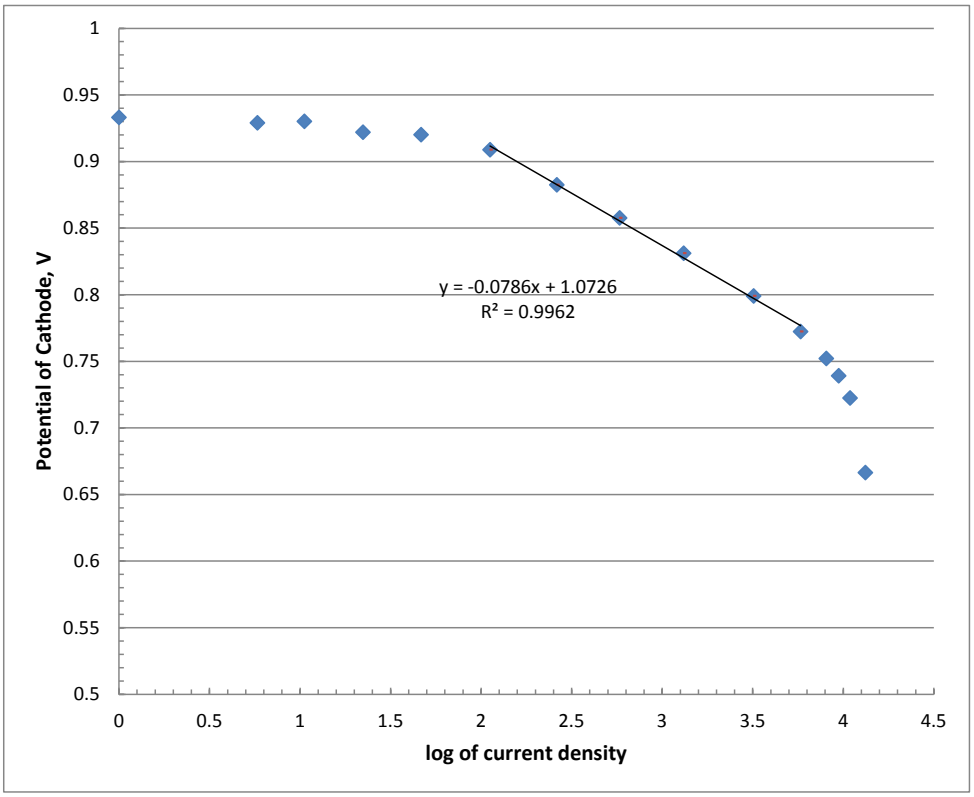
1. The following data are provided for the oxygen reduction reaction in acid media at 80 °C. The potential of the cathode, ϕ_1, is measured with respect to a hydrogen reference electrode, which in this case also serves as the counter electrode. Additionally, any ohmic resistance has been removed from the potentials tabulated.

   a. Plot these data on a semi-log plot (potential vs. log *i*). You may assume that the kinetics for the hydrogen reaction is fast, and thus the anode polarization is small. What is the Tafel slope (mV/decade) in the mid-current range?
   b. Even though ohmic polarizations have been removed, at both low and high currents, the slope is not linear on the semi-log plot. Suggest reasons why this may be the case.

I, A/m^2	ϕ_1, V	I, A/m^2	ϕ_1, V	I, A/m^2	ϕ_1, V
1	0.933	112.1	0.9087	5815	0.7722
5.83	0.929	262.3	0.8825	8081	0.7521
10.58	0.93	582.2	0.8576	9442	0.7391
22.26	0.922	1317	0.831	10905	0.7223
46.64	0.92	3201	0.799	13247	0.6664

Solution

a).



The Tafel slope is 79 mV/decade

b. At high current densities, mass transfer effects may be present. As the concentration of oxygen at the electrode decreases, the overpotential increases and the cell potential decreases. The separator of the fuel cell is not perfect, a small amount of hydrogen from the anode can dissolve and diffuse across the membrane. This hydrogen reacts with oxygen at the cathode, resulting in a small amount of oxygen reduction even in the absence of external current flow. Furthermore, because the ORR is so sluggish, there is a large overpotential even for a small amount of hydrogen crossover.

One common fuel-cell type is the solid oxide fuel cell, which uses a solid oxygen conductor in place of an aqueous solution for the electrolyte. The two reactions are

$$O_2 + 4e^- \leftrightarrow 2O^{2-}, \quad U=0.99 \text{ V}$$

and at the positive electrode

$$H_2 + O^{2-} \leftrightarrow H_2O + 2e^-, \quad U=0\text{V}$$

I, A m^{-2}	V_{cell}, V
-6981	1.5006
-4871	1.3554
-2946	1.2074
-967	1.0549
930	0.9047
2799	0.7545
4753	0.6020
6836	0.4518
9328	0.3000

Data for the polarization of a solid oxide fuel cell/electrolyzer are provided in the table. These potentials are the measured cell potentials, although the anodic overpotential is small and can be neglected. The temperature of operation is 973 K. The ohmic resistance of the cell is 0.067 Ω-cm^2. After removing ohmic polarization, how well can the reaction rate for oxygen be represented by a Butler-Volmer kinetic expression? Comment of the values obtained

Neglecting the polarization at the anode,

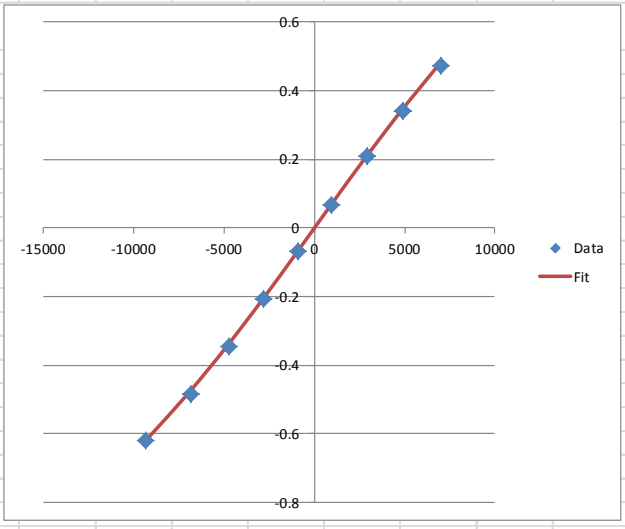
$$V_{\text{cell}} = V_{\text{oc}} - IR_\Omega - \eta_{\text{cath}}$$

$$\eta_{\text{cath}} = V_{\text{oc}} - IR_\Omega - V_{\text{cell}}$$

use V_{oc}=0.98 V

Make the correction for IR, plot the cathode polariztion as a function of current density and fit with the Butler-Volmer equation

		F/RT	11.92716													
	0.59	c	0.106999													
	0.42	i	5336.409													
	0.41	a	0.508697													
	U=0.98															
iR free	overpotential	Current density	calculated current		error											
1.453849	0.473849	6980.82	6854.746		-126.074274											
1.322727	0.342727	4870.62	4818.432		-52.1881704											
1.322727	0.342727	4870.62	4818.432		-52.1881704											
1.187634	0.207634	2945.71	2861.317		-84.3930802											
1.04839	0.06839	967.119	932.7028		-34.4161899											
0.910956	-0.06904	-930.026	-941.638		-11.6124641											
0.773292	-0.20671	-2798.88	-2848.26		-49.3774323											
0.633852	-0.34615	-4753.22	-4869.61		-116.39143											
0.497573	-0.48243	-6836.36	-6994.03		-157.673831											
0.362492	-0.61751	-9328.21	-9308.87		19.33507643											
					71003.42638											



We obtain the following,

$$i_o = 5336 \text{ A m}^{-2}$$
$$\alpha_a = 0.51$$
$$\alpha_c = 0.11$$

The fit is reasonable, but the reaction is a four electron reaction, and we would expect that $\alpha_a + \alpha_a = 4$, which is clearly not the case. Even though the fit is ok, there is no reason to believe that the mechanism is represented by the Butler-Volmer equation.

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PROBLEM 3-17

hydrogen gassing from Lead acid cell

$F = 96485$ [Coulomb/mol]

$R = 8.314$ [J/mol-K]

$T = 308.15$ [K]

$$frt = \frac{F}{R \cdot T}$$

$te = 2$ *temperature effect*

negative electrode of lead acid cell

$io_n = te \cdot 100$ [A/m^2]

phi$_1$=-0.44$_V$

$I + Ih = -495.2$ [A/m^2] *value calculated in problem 3b*

$Un = -0.356$ [V]

$\eta_n = \phi_1 - Un$

$$I = io_n \cdot \left[\mathbf{exp}\left(0.5 \cdot \eta_n \cdot frt\right) - \mathbf{exp}\left(-0.5 \cdot \eta_n \cdot frt\right) \right]$$

add hydrogen reaction

io$_h$=6.6e-10 [A/m^2];

pure Pb

$io_h = te \cdot 0.0003715$ [A/m^2] *Pb-Sb*

$Uh = 0$ [V]

$\eta_h = \phi_1 - Uh$

$$Ih = io_h \cdot \left[\mathbf{exp}\left(0.5 \cdot \eta_h \cdot frt\right) - \mathbf{exp}\left(-0.5 \cdot \eta_h \cdot frt\right) \right]$$

calculate current efficiency

$$\eta_c = \frac{I}{I + Ih}$$

current efficiency at 298

eta$_c$=0.9961, phi=-0.44V,

SOLUTION

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Unit Settings: SI C kPa kJ mass deg

η_c = 0.9965
η_n = -0.05509 [V]
frt = 37.66 [1/V]
Ih = -1.709 [A/m^2]
io_n = 200 [A/m^2]
R = 8.314 [J/mol-K]
te = 2
Un = -0.356 [V]

η_h = -0.4111 [V]
F = 96485 [Coulomb/mol]
I = -493.5 [A/m^2]
io_h = 0.000743 [A/m^2]
ϕ_1 = -0.4111 [V]
T = 308.2 [K]
Uh = 0 [V]

No unit problems were detected.

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Problem 3-18

$MW = 0.32924$ [kg/mol]

$T = 298.15$ [K]

$R = 8.314$ [J/mol-K]

$F = 96485$ [coulomb/mol]

$m = 0.00001$ [kg]

$V = 0.0001$ [m^3]

$$c_K = 3 \cdot \frac{m}{MW \cdot V}$$

$$c_{ferri} = c_{ferro}$$

$$c_{ferro} = 0.5 \cdot \frac{m}{MW \cdot V}$$

$U^o = 0.26$ [V] *because potential is at std potential, the concentration of ferri and ferro are the same*

$U = U^o + a$

$a = 0.01$ [V]

$$a = R \cdot \frac{T}{F} \cdot \ln\left[\frac{cn_{ferri}}{cn_{ferro}}\right]$$

$$cn_{ferri} + cn_{ferro} = 2 \cdot c_{ferri}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$a = 0.01$ [V]
$cn_{ferri} = 0.1811$ [mol/m^3]
$cn_{ferro} = 0.1227$ [mol/m^3]
$c_{ferri} = 0.1519$ [mol/m^3]
$c_{ferro} = 0.1519$ [mol/m^3]
$c_K = 0.9112$ [mol/m^3]
$F = 96485$ [coulomb/mol]
$m = 0.00001$ [kg]
$MW = 0.3292$ [kg/mol]
$R = 8.314$ [J/mol-K]
$T = 298.2$ [K]
$U = 0.27$ [V]
$U^o = 0.26$ [V]
$V = 0.0001$ [m^3]

No unit problems were detected.

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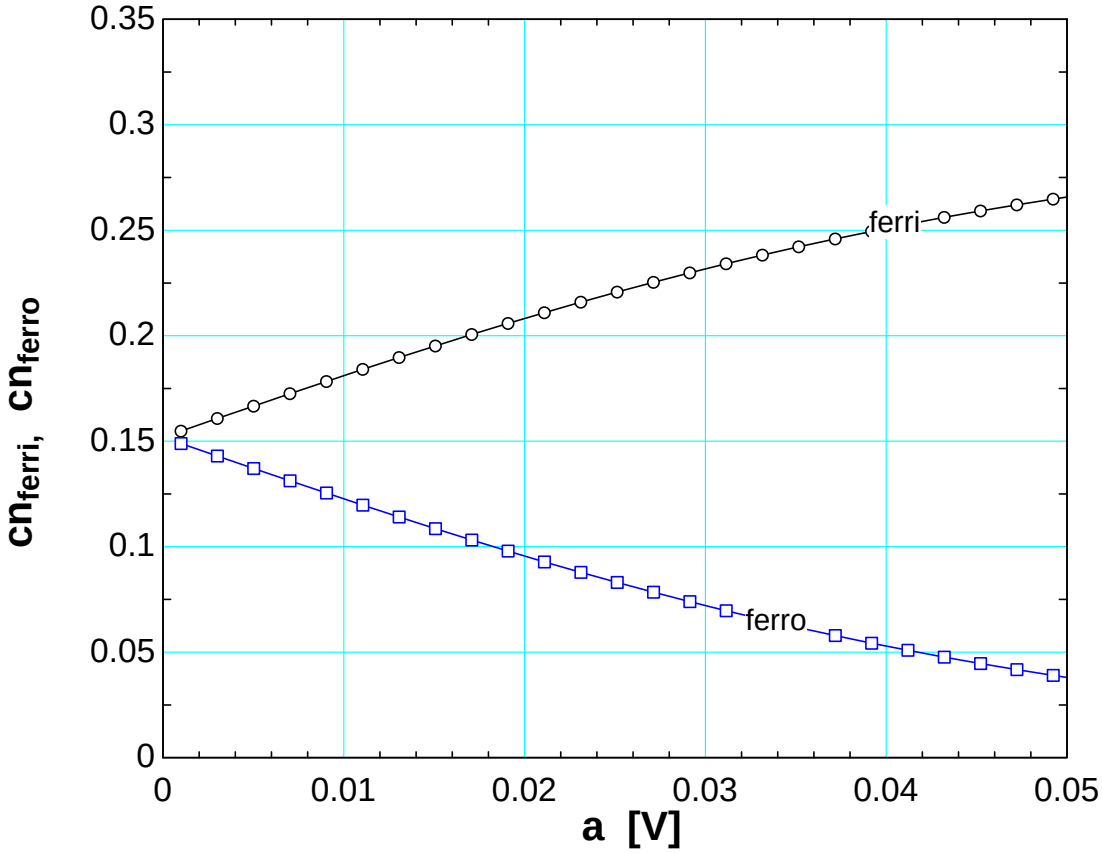

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PROBLEM 4-1

$n = 4$

$F = 96485$ [Coulomb/mol]

$D = 2.1 \times 10^{-10}$ [m^2/s]

$cs = 3$ [mol/m^3]

$L = 0.000005$ [m]

$$i_{lim} = n \cdot F \cdot D \cdot \frac{cs}{L}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cs = 3 [mol/m^3]
F = 96485 [Coulomb/mol]
L = 0.000005 [m]
D = 2.100E-10 [m^2/s]
i_{lim} = 48.63 [A/m^2]
n = 4

No unit problems were detected.

For a binary electrolyte show that the electric field can be eliminated and equation 4-19 results.

Start with differential mass balance

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \boldsymbol{N}_i + \mathcal{R}_i$$

and Nernst Planck equation

$$\boldsymbol{N}_i = -z_i u_i F c_i \nabla\phi - D_i \nabla c_i + c_i \mathbf{v}$$

For a binary electrolyte, combine and write for anion and cation, assume no homogeneous reaction

$$\frac{\partial c_+}{\partial t} = z_+ u_+ F \nabla \cdot (c_i \nabla\phi) + D_+ \nabla^2 c_+ - \nabla \cdot (c_+ \mathbf{v})$$

since $c_+ = \nu_+ c$

$$\frac{\partial c}{\partial t} = z_+ u_+ F \nabla \cdot (c \nabla\phi) + D_+ \nabla^2 c - \nabla \cdot (c \mathbf{v})$$

for incompressible fluid $\nabla \cdot \mathbf{v} = \mathbf{0}$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = z_+ u_+ F \nabla \cdot (c \nabla\phi) + D_+ \nabla^2 c$$

and

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = z_- u_- F \nabla \cdot (c \nabla\phi) + D_- \nabla^2 c$$

subtract these two

$$(z_+ u_+ - z_- u_-) F \nabla \cdot (c \nabla\phi) + (D_+ + D_-) \nabla^2 c = 0$$

rearrange to solve for the potential

$$F \nabla \cdot (c \nabla\phi) = \frac{(D_+ + D_-) \nabla^2 c}{(z_+ u_+ - z_- u_-)}$$

which is substituted back into the material balance to eliminate the potential.

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = z_+ u_+ F \nabla \cdot \frac{(D_+ + D_-) \nabla^2 c}{(z_+ u_+ - z_- u_-)} + D_+ \nabla^2 c$$

or

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \left\{ \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-} \right\} \nabla^2 c$$

Define

$$D = \left\{ \frac{D_+ D_- (z_+ - z_-)}{z_+ D_+ - z_- u D_-} \right\}$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = D \nabla^2 c$$

At the positive electrode of a lead-acid battery the reaction is

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$$

a. If the electrolyte is treated as a binary system consisting of H^+ and SO_4^{2-}, show that at the surface the current is given by

$$\frac{i}{F} = \frac{-2D}{2 - t_+}\frac{\partial c}{\partial x}$$

b. What issues could arise from the formation of solid lead sulfate on the surface?

$$i = F\sum z_i N_i = F(z_+ N_+ + z_- N_-)$$

From the stoichiometry of the reaction

$$N_+ = 4N_-$$

$$i = F\left(N_+ - (2)\frac{N_+}{4}\right) = F\frac{N_+}{2}$$

$$N_+ = \frac{2i}{F}, \quad N_- = \frac{i}{2F}$$

$$\boldsymbol{N}_+ = \tfrac{2i}{F} = -z_+ u_+ F c_+ \tfrac{\partial \phi}{\partial x} - D_+ \tfrac{\partial c_+}{\partial x}.$$

$$\boldsymbol{N}_- = \tfrac{i}{2F} = -z_- u_- F c_- \tfrac{\partial \phi}{\partial x} - D_- \tfrac{\partial c_-}{\partial x}.$$

Eliminate the potential from these two equations, divide each equation by u_i, and add—recall that $z_- c_- + z_+ c_+ = 0$ from electroneutrality

$$\tfrac{2i}{Fu_+} + \tfrac{i}{2Fu_-} = -\tfrac{D_+}{u_+}\tfrac{\partial c_+}{\partial x} - \tfrac{D_-}{u_-}\tfrac{\partial c_-}{\partial x}.$$

Also from electroneutrality

$$\frac{-z_+}{z_-}\frac{\partial c_+}{\partial x} = \frac{\partial c_-}{\partial x}$$

$$\tfrac{2i}{Fu_+} + \tfrac{i}{2Fu_-} = -\left\{\tfrac{D_+}{u_+ z_+} - \tfrac{D_-}{u_- z_-}\right\} z_+ \tfrac{\partial c_+}{\partial x}.$$

multiply by

$$\frac{u_+ u_- z_+ z_-}{u_+ z_+ - u_- z_-}$$

$$\frac{i}{F}\left\{\frac{2u_-z_+z_-}{u_+z_+-u_-z_-}+\frac{u_+z_+z_-}{2(u_+z_+-u_-z_-)}\right\}=\left\{\frac{D_-u_+z_+-D_+u_-z_-}{u_+z_+-u_-z_-}\right\}z_+\frac{\partial c_+}{\partial x}.$$

$$\frac{i}{F}\left\{-2z_+t_-+\frac{1}{2}t_+z_-\right\}=Dz_+\frac{\partial c_+}{\partial x}=2Dz_+\frac{\partial c}{\partial x}.$$

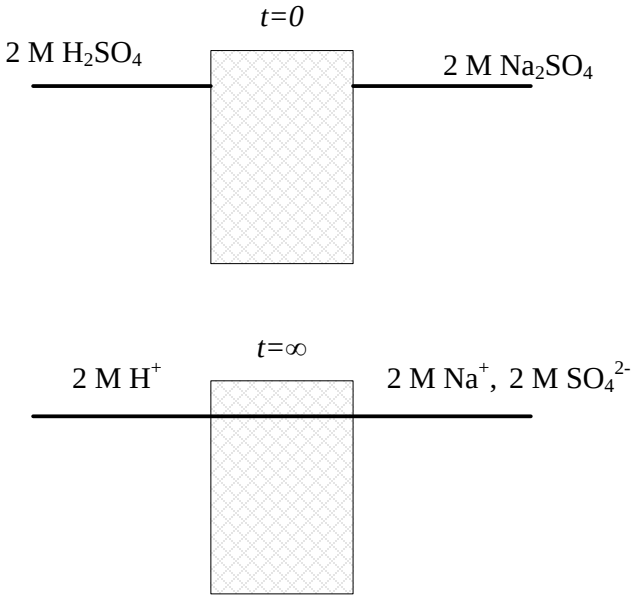
$$\frac{i}{F}\left\{-2z_+(1-t_+)+\frac{1}{2}t_+z_-\right\}=2Dz_+\frac{\partial c}{\partial x}.$$

$$\frac{i}{F}(-2+t_+)=2D\frac{\partial c}{\partial x}.$$

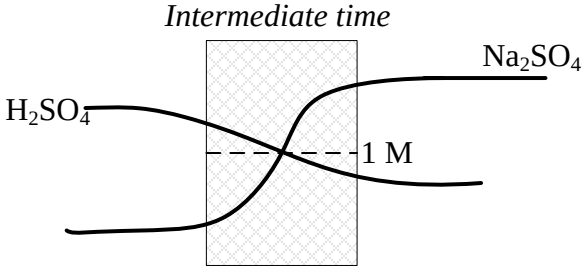
$$\boxed{\frac{i}{F}=\frac{-2D}{(2-t_+)}\frac{\partial c}{\partial x}}$$

A porous film separates two solutions. The left side contains 2M sulfuric acid, whereas on the right side there is 2M Na_2SO_4. Discuss the rate of transport of sulfate ions across the membrane and the final equilibrium state.

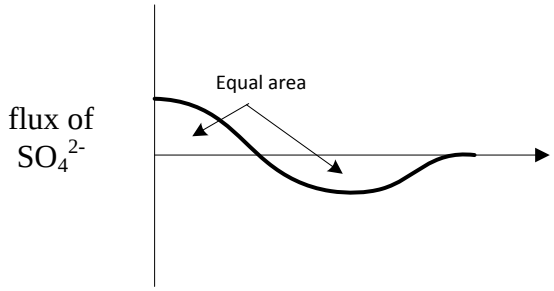
The situation is reflected in the figure below showing initial and final states. It is assumed that the volumes of the two compartments are the same and that the salts are fully dissociated. Further, the volume of the separator is neglected. In the final state, the concentration of each of the ions will be 2 M, corresponding to a concentration of 1 M H_2SO_4 and 1 M Na_2SO_4



Although initial and final sulfate ion concentrations are the same, they are not constant over time. This behavior is best understood by noting that H^+ and Na^+ will have different mobilities. The conduction per equivalent (λ_+, which is proportional to the mobility) of H^+ is more than six times larger than that of Na^+. Because of electroneutrality, the flux of anions and cations are coupled. If we view the diffusing species as H_2SO_4 and Na_2SO_4, at some intermediate time the concentration profiles are shown below. The concentration of sulfuric acid will more quickly reach a constant 1 M, whereas the Na_2SO_4 will diffuse more slowly.



If we were to plot the flux of sulfate ions through the separator as a function of time it might look something like this



Initially, the flux is positive corresponding to the rapid diffusion of sulfuric acid. At longer times, the flux becomes negative after the sulfuric acid is nearly equilibrated and the sodium sulfate diffusion continues. The area under the curve should be zero.

The purpose of this problem is to compare the limiting current for the electrorefining of copper both with and without supporting electrolyte. Assume that copper is reduced at the left electrode ($x = 0$) and oxidized at the right electrode ($x=L$). You should also assume steady state and no convection. Finally, assume that the current efficiency for both copper oxidation and reduction are 100 %. (Note that the assumption of no convection leads to very low values of the limiting current since transport by diffusion is slow over the 5 cm cell gap).

a. Derive an expression for the limiting current as a function of the diffusivity, the initial concentration of copper (which is also the average concentration), and the cell gap, L.
b. Derive an analogous expression for the limiting current in the presence of a supporting electrolyte.
c. How do the two expressions compare? Why is the limiting current lower in the presence of a supporting electrolyte?
d. For the binary system, derive an expression for the concentration profile as a function of current for values below the limiting current. What is the sign of the current in this expression?

a)

$$\boldsymbol{N}_- = 0 = -z_- u_- F c_- \frac{\partial \phi}{\partial x} - D_- \frac{\partial c_-}{\partial x}.$$

$$\frac{\partial \phi}{\partial x} = \frac{-D_-}{z_- u_- F c_-} \frac{\partial c_-}{\partial x}$$

$$\boldsymbol{N}_+ = -z_+ u_+ F c_+ \frac{\partial \phi}{\partial x} - D_+ \frac{\partial c_+}{\partial x}.$$

substitute for the gradient in potential

$$\boldsymbol{N}_+ = -D_+ \frac{\partial c_+}{\partial x} + z_+ u_+ F c_+ \left(\frac{D_-}{z_- u_- F c_-} \frac{\partial c_-}{\partial x} \right).$$

use

$$c_+ = \nu_+ c, \text{ and } c_- = \nu_- c$$

and

$$D_i = RT u_i$$

$$\boldsymbol{N}_+ = D_+ \frac{\partial c_+}{\partial x} \left\{ -\nu_+ + \frac{z_+}{z_-} \nu_+ \right\} = -\nu_+ D_+ \frac{\partial c_+}{\partial x} \left(1 - \frac{z_+}{z_-} \right)$$

Then, find the limiting current for a binary electrolyte $CuSO_4$.

$$i_{lim} = nF N_+ = D_+ \frac{(c_+ - 0)}{L} \left\{ 1 - \frac{2}{-2} 1 \right\} = \boxed{\frac{2nF D_+ c_+}{L}}$$

b) with the supporting electrolyte, the electric field is small and migration is neglected. $\boldsymbol{N}_+ = -D_+ \frac{\partial c_+}{\partial x}$

$$\boxed{i_{lim} = \frac{nF D_+ c_+}{L}}$$

c) Migration is driving Cu^{2+} in the same direction as the concentration gradient. The two driving forces, Δc and $\Delta\phi$ add together. In the presence of migration, the limiting current is doubled.

d) We expect a linear profile in concentration. Because the total amount of salt is constant, its concentration at the center is unchanged, c^o.

at $x=L/2$ $c= c^o$

at $x=0$ $c = \left(1 + {}^{i}/_{i_{lim}}\right) c^o$

assuming a linear change in concentration

$$c = \left(1 + {}^{i}/_{i_{lim}}\right) c^o - \frac{2c^o}{L}\left({}^{i}/_{i_{lim}}\right) x$$

$$\boxed{\frac{c}{c^o} = 1 + {}^{i}/_{i_{lim}}\left(1 - {}^{2x}/_{L}\right)}$$

One type of Li-ion battery includes a graphite negative electrode and manganese-dioxide spinel positive electrode, described by the following reactions (written in the discharge direction)

$$\mathrm{Li}_x\mathrm{C}_6 \rightarrow x\mathrm{Li}^+ + x\mathrm{e}^- + \mathrm{C}_6 \quad \text{(negative)}$$
$$x\mathrm{Li}^+ + x\mathrm{e}^- + \mathrm{Mn}_2\mathrm{O}_4 \rightarrow \mathrm{Li}_x\mathrm{Mn}_2\mathrm{O}_4 \quad \text{(positive)}$$

The electrolyte consists of an organic solvent that contains a binary $LiPF_6$ lithium salt, where the anion is PF_6^-. Assume a 1D cell with the cathode located at x=0 and the anode located at x=L. The following properties are known:

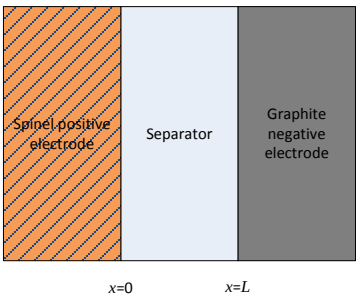
$$D_{\mathrm{Li}^+} = 1.8 \times 10^{-10} \ \mathrm{m^2 s^{-1}}$$
$$D_{\mathrm{PF_6}^-} = 2.6 \times 10^{-10} \ \mathrm{m^2 s^{-1}}$$

$$t_+ = 0.4$$

For our purposes here, we assume that the electrodes are flat surfaces, and that they are separated by an electrolyte-containing separator that is 25 μm thick. The initial concentration of $LiPF_6$ in the electrolyte is 1.0 M. The parameters given above are for transport in the separator. The same expression derived in the text for the concentration also applies to this situation, equation 4-39.

a. In which direction does the current in solution flow during discharge? Is this positive or negative relative to the x direction?
b. Where is the concentration highest, at x=0 or x=L?
c. What is the concentration difference across the separator if a cell with a 2cm x 5cm electrode is operated at a current of 10mA? Is this difference significant?
d. Briefly describe how you would calculate the cell potential for a constant current discharge of this cell if the current is known and the concentration variation is known. The potential that would be measured between the current collectors of the cathode and anode during discharge. You do <u>not</u> need to include all the equations that you would use. The important thing is that you know and are able to identify the factors that contribute to the measured cell potential, and that you know the process by which you might determine their values.

a)



During discharge Li+ ions move from the negative electrode to the positive electrode. For the coordinate system defined, the current is negative.

b) The concentration of salt is highest at x=L. You can reach this conclusion by considering the flux of the anion. Since the anion is not involved in the reactions, its flux is zero at steady state. Based on current flow (negative), the potential gradient is positive, and migration would push

negatively charged species up the gradient. In order for the flux to be zero, a concentration gradient is established to drive flow in the opposite direction. Therefore, the concentration is highest at the negative electrode.

c) $$c = \frac{i}{F}\frac{(1-t_+)}{D}\left[{}^{L}/_{2} - x\right] + c^o \qquad (4\text{-}39)$$

$$\Delta c = c(L) - c(0) = \frac{i}{F}\frac{(1-t_+)}{D}\left[-{}^{L}/_{2} - {}^{L}/_{2}\right]$$

$D_i = RTu_i$, and using the diffusivity values

$$t_+ = \frac{z_+u_+}{z_+u_+ - z_-u_-} = \frac{D_+}{D_+ + D_-} = 0.41$$

$$D = \frac{z_+u_+D_- - z_-u_-D_+}{z_+u_+ - z_-u_-} = \frac{2D_+D_-}{D_+ + D_-} = 2.13 \times 10^{-10}\ \text{m}^2\ \text{s}^{-1}$$

$$\Delta c = \frac{0.01}{(0.001)F}\frac{(1-0.41)}{2.13 \times 10^{-10}}[25 \times 10^{-6}] = 7.2\ \text{mol m}^{-3}$$

d)

$$V_{cell} = U - \eta_\Omega - |\eta_{\text{anode}}| - |\eta_{\text{anode}}|$$

$$\eta_\Omega = \left|\frac{iL}{\kappa}\right|$$

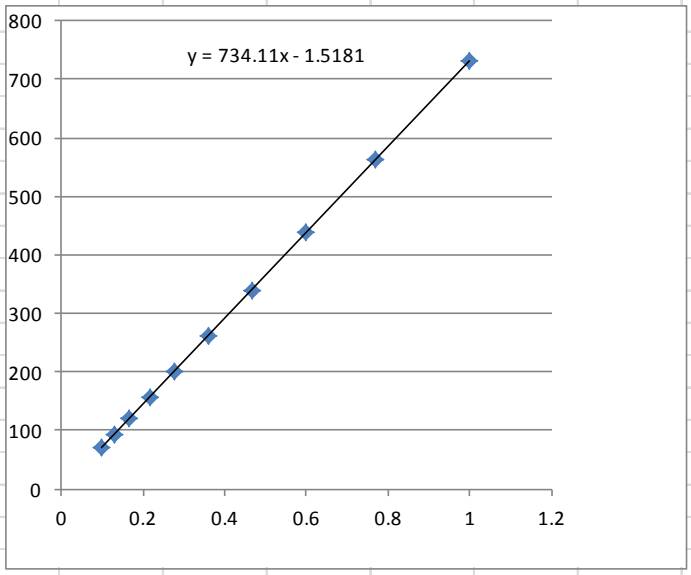
The concentration of the salt at the negative and positive electrodes is determined as described in part (b). The kinetic polarizations would then be determined at each electrode. These three polarizations are subtracted from the equilibrium potential to arrive at the potential of the cell.

A potential step experiment is conducted on a solution of 0.5 M $K_3Fe(CN)_6$, and 0.5 M Na_2CO_3 . The potential is large enough so that the reduction of ferricyanide is under diffusion control. Using the data provided, estimate the diffusion coefficient of the ferricyanide.

$$\left[Fe(CN)_6\right]^{3-} + e^- \rightarrow \left[Fe(CN)_6\right]^{4-} \qquad (U^{\theta}=0.3704\ V)$$

Create a plot of the current versus the reciprocal of the square root of time. See illustration 4.2

time, s	sqrt time	I, A/m2
1	1	731
1.7	0.766965	564
2.8	0.597614	438
4.6	0.466252	340
7.7	0.360375	263
12.9	0.278423	201
21.5	0.215666	156
35.9	0.166899	122
59.9	0.129207	94
100	0.1	72



Then use the Cottrell equations

$$i = \frac{nF\sqrt{D_i}c_i^{\infty}}{\sqrt{\pi}}\frac{1}{\sqrt{t}}$$

using slope from the fit

$$\frac{nF\sqrt{D_i}c_i^{\infty}}{\sqrt{\pi}} = 734.11$$

Solve for the diffusivity

$$D = 7.3 \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$$

Platinum is used as a catalyst for oxygen reduction in low-temperature, acid fuel cells. At high potentials, the platinum is unstable and can dissolve, (See problem 2-17), though the concentration of Pt^{2+} is quite small. The electrolyte conductivity is 10 S m^{-1}, and the current density, carried by protons, is 100 A m^{-2}. Assume the temperature is 80 °C and that the Pt^{2+} is transported over a distance of 20 μm, is it reasonable to neglect migration when analyzing the transport of platinum ions?

Using the Nernst-Planck equation, compare the magnitudes of the terms for diffusion and migration.

$$\mathbf{N}_i = \underbrace{-z_i u_i F c_i \nabla \phi}_{\text{migration}} \underbrace{- D_i \nabla c_i}_{\text{diffusion}} \underbrace{+ c_i \mathbf{v}}_{\text{convection}} . \tag{4-3}$$

$$\frac{|D_i \nabla c_i|}{|u_i \mathrm{F} z_i c_i \nabla \phi|}$$

Apply the Nernst-Einstein relation, $D_i = u_i RT$

At limiting current, $\nabla c_i \approx \frac{c_i}{L}$ and from Ohm's law $\nabla \phi \approx \frac{i}{\kappa}$

$$\frac{|D_i \nabla c_i|}{|u_i \mathrm{F} z_i c_i \nabla \phi|} = \frac{u_i RT \, {c_i}/{L}}{u_i \mathrm{F} z_i c_i \, {i}/{\kappa}} = \frac{RT}{F} \frac{\kappa}{z_i L i} = 76$$

Compared to diffusion, migration is a small contributor to the flux of platinum ions.

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PROBLEM 4-9

0.05 M KOH

$c = 50$ [mol/m^3]

$F = 96485$ [coulomb/mol]

$R = 8.314$ [J/mol-K]

$T = 298.15$ [K]

$zp = 1$

$zn = -1$

$nup = 1$

$nun = 1$

$cp = nup \cdot c$

$cn = nun \cdot c$

$\lambda_p = 0.007352$ [m^2/Ω-mol]

$\lambda_n = 0.01976$ [m^2/Ω-mol]

$\lambda_p = up \cdot F \cdot F \cdot |zp|$

$\lambda_n = un \cdot F \cdot F \cdot |zn|$

conductivity

$\kappa = F \cdot F \cdot [zp \cdot zp \cdot up \cdot cp + zn \cdot zn \cdot un \cdot cn]$

transference number

$$tp = zp \cdot zp \cdot up \cdot \left[\frac{cp}{zp \cdot zp \cdot up \cdot cp + zn \cdot zn \cdot un \cdot cn}\right]$$

salt diffusivity

$Dp = R \cdot T \cdot up$

$Dn = R \cdot T \cdot un$

$$D = \frac{zp \cdot up \cdot Dn - zn \cdot un \cdot Dp}{zp \cdot up - zn \cdot un}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$c = 50$ [mol/m^3]

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$c_n = 50$ [mol/m^3]
$c_p = 50$ [mol/m^3]
$D = 2.854E-09$ [m^2/s]
$D_n = 5.262E-09$ [m^2/s]
$D_p = 1.958E-09$ [m^2/s]
$F = 96485$ [coulomb/mol]
$\kappa = 1.356$ [1/Ω-m]
$\lambda_n = 0.01976$ [m^2/Ω-mol]
$\lambda_p = 0.007352$ [m^2/Ω-mol]
$n_{un} = 1$
$n_{up} = 1$
$R = 8.314$ [J/mol-K]
$T = 298.2$ [K]
$t_p = 0.2712$
$u_n = 2.123E-12$ [mol-m^2/(coulomb^2-Ω)]
$u_p = 7.897E-13$ [mol-m^2/(coulomb^2-Ω)]
$z_n = -1$
$z_p = 1$

No unit problems were detected.

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PROBLEM 4-10

0.10 M CuSO4

$c = 100$ [mol/m^3]

$F = 96485$ [coulomb/mol]

$R = 8.314$ [J/mol-K]

$T = 298.15$ [K]

$zp = 2$

$zn = -2$

$nup = 1$

$nun = 1$

$cp = nup \cdot c$

$cn = nun \cdot c$

$\lambda_p = 0.0054$ [m^2/Ω-mol]

$\lambda_n = 0.008$ [m^2/Ω-mol]

$\lambda_p = up \cdot F \cdot F \cdot |zp|$

$\lambda_n = un \cdot F \cdot F \cdot |zn|$

conductivity

$\kappa = F \cdot F \cdot [zp \cdot zp \cdot up \cdot cp + zn \cdot zn \cdot un \cdot cn]$

transference number

$$tp = zp \cdot zp \cdot up \cdot \left[\frac{cp}{zp \cdot zp \cdot up \cdot cp + zn \cdot zn \cdot un \cdot cn}\right]$$

salt diffusivity

$Dp = R \cdot T \cdot up$

$Dn = R \cdot T \cdot un$

$$D = \frac{zp \cdot up \cdot Dn - zn \cdot un \cdot Dp}{zp \cdot up - zn \cdot un}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$c = 100$ [mol/m^3]

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cn = 100 [mol/m^3]
cp = 100 [mol/m^3]
D = 8.584E-10 [m^2/s]
Dn = 1.065E-09 [m^2/s]
Dp = 7.189E-10 [m^2/s]
F = 96485 [coulomb/mol]
κ = 2.68 [1/Ω-m]
λ_n = 0.008 [m^2/Ω-mol]
λ_p = 0.0054 [m^2/Ω-mol]
nun = 1
nup = 1
R = 8.314 [J/mol-K]
T = 298.2 [K]
tp = 0.403
un = 4.297E-13 [mol-m^2/(coulomb^2-Ω)]
up = 2.900E-13 [mol-m^2/(coulomb^2-Ω)]
zn = -2
zp = 2

No unit problems were detected.

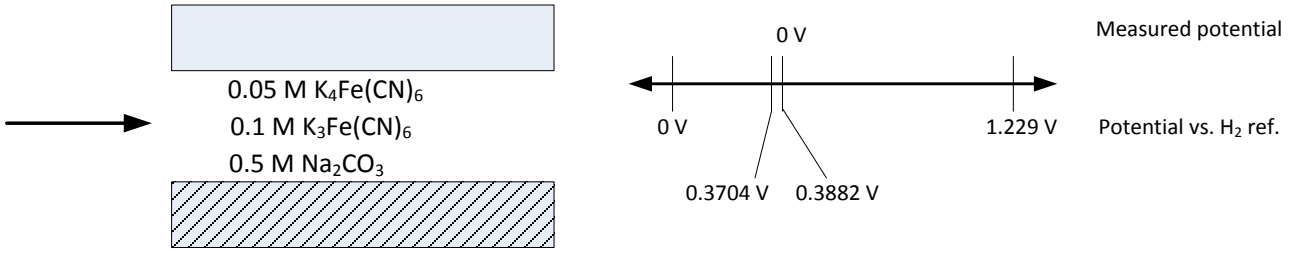
An electrochemical process is planned where there is flow between two parallel electrodes. In order to properly design the system, an empirical correlation for the mass-transfer coefficient is sought. An aqueous solution containing 0.05 M $K_4Fe(CN)_6$, 0.1 M, M $K_3Fe(CN)_6$, and 0.5 M Na_2CO_3 is circulated between the electrodes. The reaction at the electrodes is

$$\left[Fe(CN)_6\right]^{3-} + e^- \leftrightarrow \left[Fe(CN)_6\right]^{4-} \qquad (U^{\theta}=0.3704 \text{ V})$$

a. If the potential difference between electrodes is increased slowly from zero, sketch the current voltage relationship that would result. Include on the graph, the equilibrium potential for the reaction, the open-circuit potential, the limiting current, and the decomposition of water.

b. For the conditions provided, which electrode would you expect to reach the limiting current first?

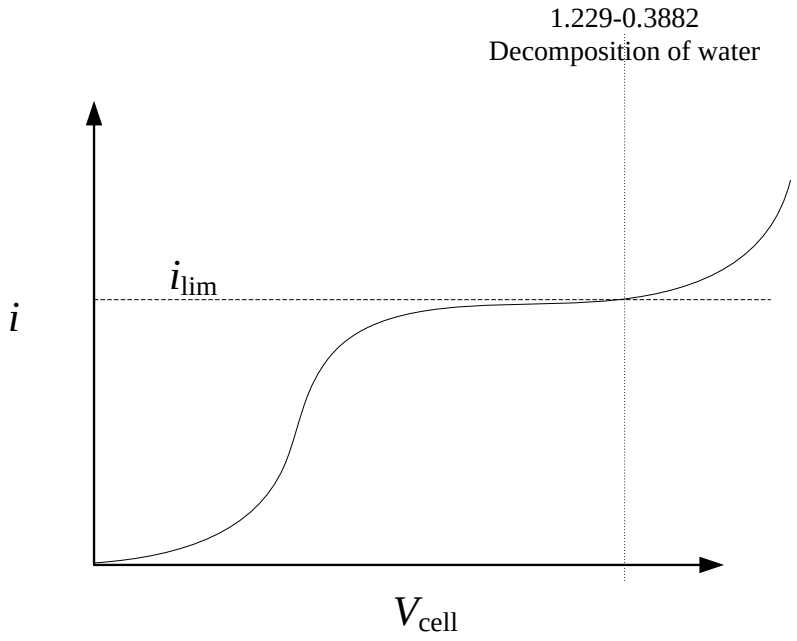
c. Show how to calculate a mass-transfer coefficient, k_c, from these limiting current data.



a) Assuming that the same reactions occur at each electrode, at open circuit, there is no potential difference between the electrodes, V_{cell}=0. The equilibrium (thermodynamic) potential of either electrode relative to a hydrogen reference is obtained with the Nernst equation.

$$U = U^{\theta} - \frac{RT}{nF}\ln\frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_6^{3-}]}$$

$$U = 0.3704 - \frac{RT}{(1)F}\ln\frac{[0.05]}{[0.10]} = 0.3882 \text{ V}$$



b) The two reactions are

$$\mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(CN)_6^{3-}} + \mathrm{e^-} \qquad \text{anode}$$

$$\mathrm{Fe(CN)_6^{3-}} + \mathrm{e^-} \rightarrow \mathrm{Fe(CN)_6^{4-}} \qquad \text{cathode}$$

The ferri-cyanide is at a lower concentration, and therefore the anode would reach a limiting current sooner.

c) Calculate the mass-transfer coefficient from the limiting current,

$$i_{lim} = nFk_c c_i^{\infty}$$

Then calculate the Sherwood, it is this dimensionless number that would be used to develop a correlation

$$\mathrm{Sh} = \frac{k_c L}{D} = \frac{i_{lim} L}{nF c_i^{\infty} D}$$

For the system described in problem 4.11,

a. use the data provided for I_{lim} versus flow rate to develop a correlation for dimensionless mass-transfer coefficient, Sh. The Re should be defined with the hydraulic diameter, $d_h = \frac{4A_c}{P}$. At 298 K, the diffusivity of the ferri/ferro cyanide is 7.2×10^{-10} m^2 s^{-1}. Treat the electrodes as 0.1m x 0.1m squares separated by a distance of 1 cm. Use as density of 998 kg m^{-3} and a viscosity of 0.001 Pa-s. Based on the literature, the following correlations are suggested.

Flowrate, cm^3/s	Limiting current, A
0.96	0.15
2.06	0.19
3.69	0.22
6.41	0.27
9.16	0.30
11.89	0.34
14.62	0.36
17.35	0.39
20.22	0.41
22.83	0.44
25.54	0.46
28.56	0.50

Laminar flow $\text{Sh} = a\text{Re}^{1/3}\text{Sc}^{1/3}\left(\frac{d_h}{L}\right)^{1/3}$

Turbulent flow $\text{Sh} = b\text{Re}^{2/3}\text{Sc}^{1/3}\left(\frac{d_h}{L}\right)^{1/4}$

b. What is the importance of the sodium carbonate in this experiment?

c. Justify the need for the additional dimensionless factor$\left(\frac{d_h}{L}\right)$.

a)

$$\text{Sh} = \frac{k_c L}{D} = \frac{i_{lim} L}{nF c_i^{\infty} D}$$

Using the data provided, calculate Sh and Re. The highest Re is about 50, therefore use the correlation for laminar flow.

$$\text{Sh} = 10.3\text{Re}^{1/3}\text{Sc}^{1/3}\left(\frac{d_h}{L}\right)^{1/3}$$

b) The sodium carbonate is added as a supporting electrolyte to reduce the ohmic loss and to allow for the elimination of migration.

c) Because the hydraulic diameter (1.8 cm) is not dramatically smaller than the length (10 cm) entrance effects are important. There are actually two important length scales in this problem, the distance between electrodes and the length of the electrodes. Had the length been much larger, entrance effects could be neglected and the only important distance would be the gap.

For the Cu electrorefining problem (see Illustration 4-7)

a. Calculate the mass-transfer coefficient, k_c (m s^{-1}) based on natural convection using the height of the electrode as the characteristic length.

b. It is desired to increase the mass transfer coefficient by a factor of 10 and thereby raise the limiting current. If forced convection is used, what fluid velocity and Re are required? The following correlations for mass transfer between parallel planes are available. The distance between the electrodes is 3 cm. Assume that the electrodes are square.

Laminar flow $\quad \mathrm{Sh} = 1.85\left(\mathrm{ReSc}\frac{d_h}{L}\right)^{1/3}$

Turbulent flow $\quad \mathrm{Sh} = 0.0789\left(\frac{0.079}{\mathrm{Re}^{0.25}}\right)^{0.5}\mathrm{ReSc}^{0.25}$

Note that in contrast to the correlation for natural convection, the Sh and Re here are based on the equivalent diameter $d_h = \frac{4A_c}{P}$.

c. For this arrangement, sparging with air at a rate of 2 L/min per square meter of electrode area results in a mass-transfer coefficient on the order of 2×10^{-5} m s^{-1}. Calculate the superficial velocity of the air and compare with the velocity obtained in part b. Why might air sparging be preferred over forced convection?

a) From illustration 4.4, Sh=3739

$$k_c = \frac{\mathrm{Sh}D}{L} = \frac{(3739)(5.33\times10^{-10})}{0.96} = 2.1\times10^{-6}\ \mathrm{m\ s^{-1}}$$

b) The goal is to have $k_c = 2.0\times10^{-5}$ m s^{-1}. First, find the equivalent diameter

$$d_h = \frac{4A_c}{P} = \frac{4LW}{2(L+W)} = \frac{2(0.96)(0.03)}{(0.96+0.03)} = 0.058\ \mathrm{m}$$

Next find the Sh number.

$$\mathrm{Sh} = \frac{k_c d_h}{D} = \frac{(2.0\times10^{-5})(0.058)}{5.33\times10^{-10}} = 2292$$

Using the correlation for turbulent flow, solve for the Re number and superficial fluid velocity.

Re=58,325 v=1.27 m s^{-1} This velocity would result in a high pressure drop.

c) $$\mathrm{v}_s = \frac{\dot{\mathbb{V}}}{A_c} = \frac{(2.0\times10^{-3})}{(1)(60\ \mathrm{s\ min^{-1}})} = 0.033\ \mathrm{m\ s^{-1}}$$

if holdup volume is 10%, the velocity is 0.3 m s^{-1} Will require less energy to sparge than to pump fluid through at high Reynolds number.

Correlations for mass-transfer coefficients for full-sized, commercial, electrowinning cells under the actual operating conditions can be difficult to measure.

a. What could be some of the challenges with measuring these mass-transfer coefficients?

b. It has been suggested [*J. Electrochem. Soc*., **121**, 867 (1974)] that k_c can be estimated by co-deposition of a trace element that is more noble. For instance in the electrowinning of Ni (U^{θ}=0.26 V), Ag (U^{θ}=0.80 V) could be used. The idea is that because the equilibrium potential for the more noble material is higher, the limiting current will be reached sooner. After a period of deposition, the electrode composition is analyzed to determine the local and average rates of mass transfer. Would the mass-transfer coefficient for Ni be the same as for Ag? If not, how would you propose correcting the measured value?

a) If the limiting current is used

- the current may be high and there may be heating effects
- large expensive equipment may be required
- the mass-transfer may be non-uniform over the surface a large electrode
- side reactions, such as the electrolysis of water, may occur--any gas bubbles generated would also change the rate of mass transfer

Measurement at a current density less than the limiting current is also difficult because the concentration of reactants would need to be measured at the surface of the electrode.

b) The mass-transfer coefficients are not the same. In general, the Sherwood number is expressed as

$$Sh = constant\ Re^{a} Sc^{b}, \qquad (4\text{-}42)$$

Given that $\mathrm{Sc} = \frac{\nu}{D}$, and $\mathrm{Sh} = \frac{k_c d_h}{D}$, where D is the diffusivity,

$$\mathrm{Sh} \propto D^{-b}$$

$$k_c \propto D^{1-b}$$

Measure the limiting current for silver deposition

$$i_{lim}^{\mathrm{Ag}} = nF k_c^{\mathrm{Ag}} c_b^{\mathrm{Ag}}$$

write similar expressions for Ni,

$$\frac{k_c^{\mathrm{Ni}}}{k_c^{\mathrm{Ag}}} = \left(\frac{D_{\mathrm{Ni}^{2+}}}{D_{\mathrm{Ag}^{+}}}\right)^{1-b}$$

For laminar flow b=⅓ and for turbulent flow b=¼.

A porous flow-through electrode has been suggested for the reduction of bromine in a Zn-Br battery.

$$Br_2 + 2e^- \rightarrow 2Br^-$$

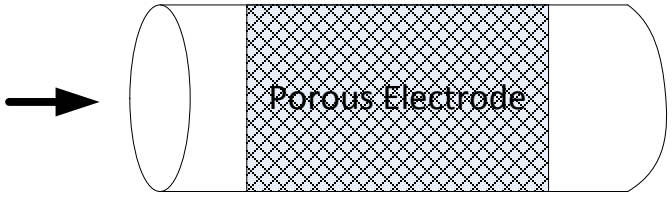
Calculate the limiting current if the bulk concentration of bromine is 5.5 mM using the correlation

$$Sh = 1.29Re^{0.72}$$

The Re is based on the diameter of the carbon particles, d_p, that make up the porous electrode.

$D_{Br_2} = 6.8x10^{-10}\ m^2/s$ $\quad v = 0.2\ cm/s$ $\quad d_p = 25\ \mu m$

$\upsilon = 9.0x10^{-7}\ m^2/s$ $\quad c^{\infty}_{Br_2} = 5.5\ mol/m^3$



First calculate Re and Sh numbers

$$Re = \frac{v d_p}{\nu} = \frac{(0.002)(25 \times 10^{-6})}{9 \times 10^{-7}} = 0.0556$$

$$Sh = 1.29Re^{0.72} = 0.161$$

Then calculate the mass transfer coefficient

$$k_c = \frac{Sh D_{Br_2}}{d_p} = 4.38 \times 10^{-6}\ m\ s^{-1}$$

$$i_{lim} = nFk_c c_{Br_2} = (2)F(4.38 \times 10^{-6})(5) = 4.65\ A\ m^{-2}$$

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```
"!Problem 4-16, mass transfer for gas evolving electrode"
t1=25 [C]
p1=100 [kPa]
rho=density(Cl2, t=t1, p=p1); "density of chlorine"
mu=viscosity(water, t=t1, p=p1); "viscosity of water"
nu=mu/rho_L; "calculation of kinematic viscosity"
Dab=1.0e-9 [m^2/s]; "diffusivity provided"
Sc=nu/Dab; "Schmidt number"


I=10000 [Coulomb/m^2-s]; "current density"
F=96487 [Coulomb/mol]
n=2
M=0.0709 [kg/mol]; "molecular weigth of chlorine gas"
Q=Vs*W*h; "volumetric flowrate of gas"

W=0.5 [m]; "width of electrode"
h=0.03 [m]; "distance between electrodes"
L=0.5 [m]; "height of electrodes"

"part a, uniform current density is assumed"
"below superficial velocity is calculated for full height, L, but L would be replaced by x to provide function of distance"
"superficial velocity increases linearly with distance from bottom of electrode"
Vs=(L*I/(n*F))*(M/rho)/h; "superficial velocity of gas"

"part b, estimate of void fraction"
"estimate terminal velocity from equation 6.7 from Treybal for bubble larger than 1.4 mm"
sigma=surfacetension(water, t=t1); "surface tensity of water"
rho_L=density(water, t=t1, p=p1)
vt=sqrt(2*sigma/(db*rho_L)+0.5*db*g#)
 Db=0.003 [m]; "assumed diameter of bubble"
 Vs=Vt*epsilon

"part c"
"Ibl approach, equation 4-50"
Ar=(g#*Db^3*epsilon)/(nu*nu*(1-epsilon))

Shi=0.19*(Ar*Sc)^0.333

Shi=kci*Db/Dab

"Fahidy approach, equation 4-49"
dh=2*W*h/(W+h)
Re=2*Q*rho/((W+h)*mu)
Sho=0;"no forced convection"
Shf=Sho+3.088*Re^0.77*Sc^0.25*(L/h)^0.336
Shf=kcf*dh/Dab

r=kci/kcf
```

SOLUTION

Unit Settings: SI C kPa kJ mass deg

Ar = 30996	Dab = 1.000E-09 [m^2/s]
db = 0.003 [m]	dh = 0.0566 [m]
ε = 0.0854	F = 96487 [Coulomb/mol]
h = 0.03 [m]	I = 10000 [$Coulomb/m^2$-s]
kcf = 0.000002186 [m/s]	kci = 0.00001905 [m/s]
L = 0.5 [m]	M = 0.0709 [kg/mol]
μ = 0.0008905 [Pa-s]	n = 2

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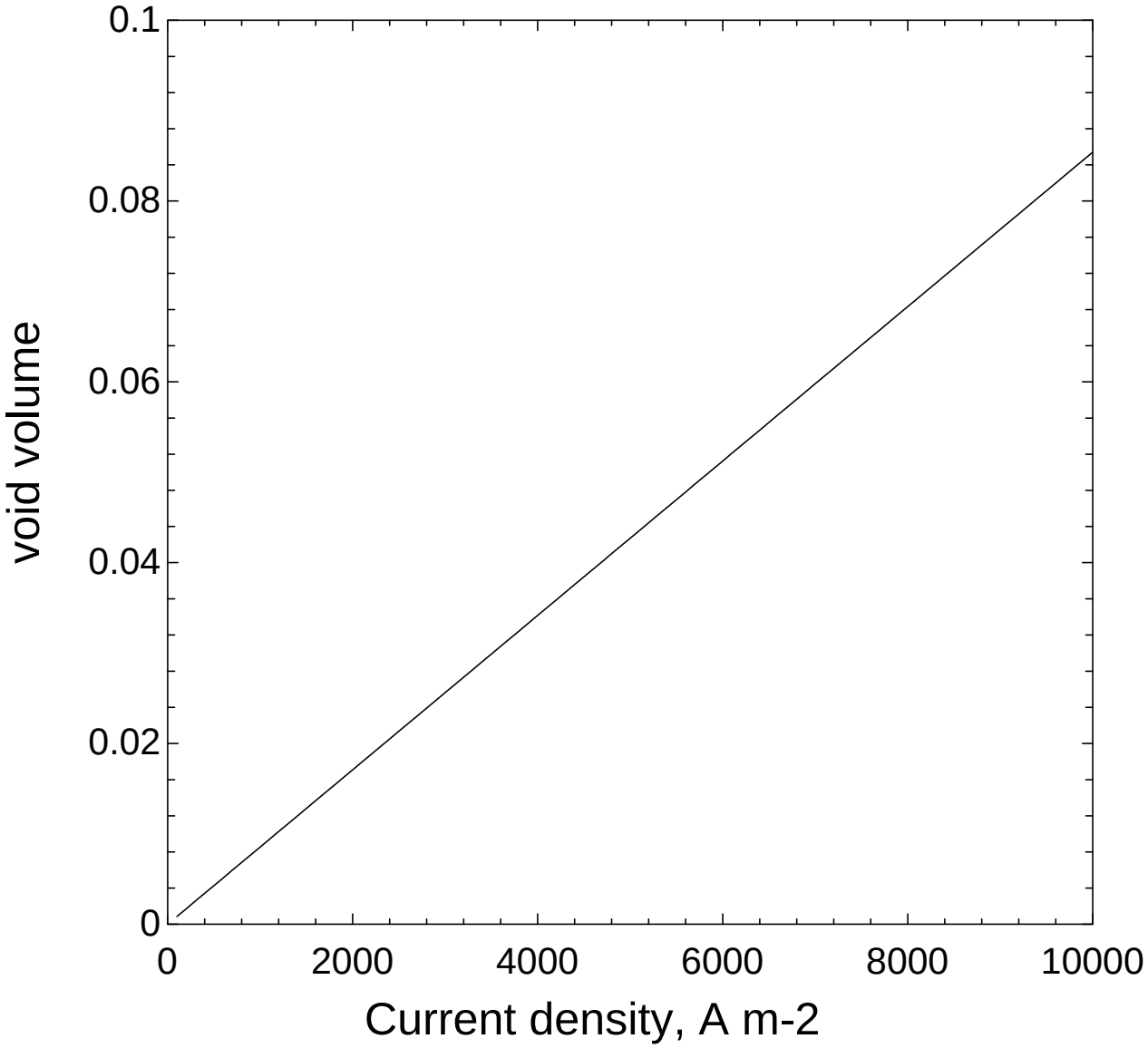
ν = 8.931E-07 [m^2/s]
Q = 0.0003211 [m^3/s]
Re = 3.892
ρ_L = 997.1 [kg/m^3]
Shf = 123.7
Sho = 0
t1 = 25 [C]
Vt = 0.2507 [m/s]

p1 = 100 [kPa]
r = 8.716
ρ = 2.86 [kg/m^3]
Sc = 893.1
Shi = 57.15
σ = 0.07197 [J/m^2]
Vs = 0.02141 [m/s]
W = 0.5 [m]

No unit problems were detected.



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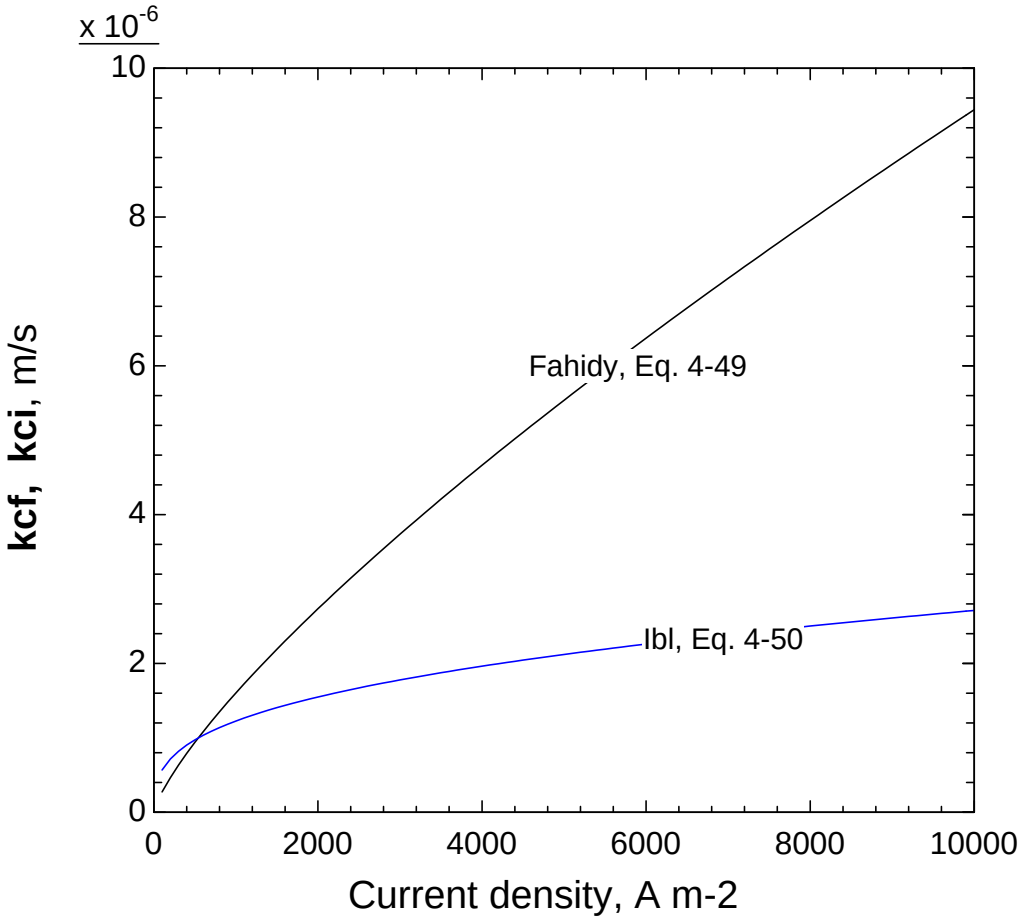
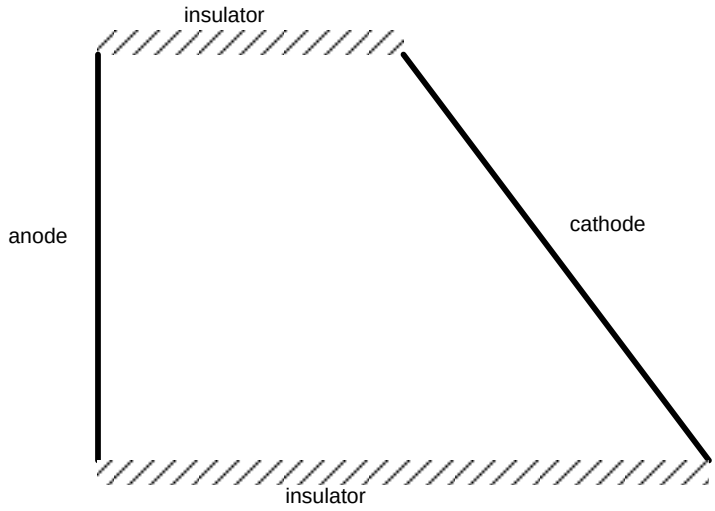
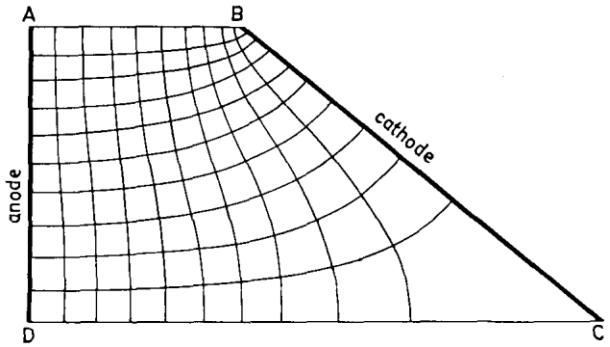


The Hull cell is used to assess the ability of a plating bath to deposit coatings uniformly, this is known as the “throwing power” of the bath. The cell shown below has two electrodes that are not parallel. The other sides of the cell are insulating. The electrodeposition of a metal is measured on the long side (cathode), and the more uniform the coating the better the throwing power.

Sketch the potential and current distribution assuming a primary current distribution.



The current and potential are sketched in the figure on the left. Also shown on the right (not required) is the primary current distribution along the cathode. This is from *J. Electrochem. Soc*., **134**, 3015 (1987).



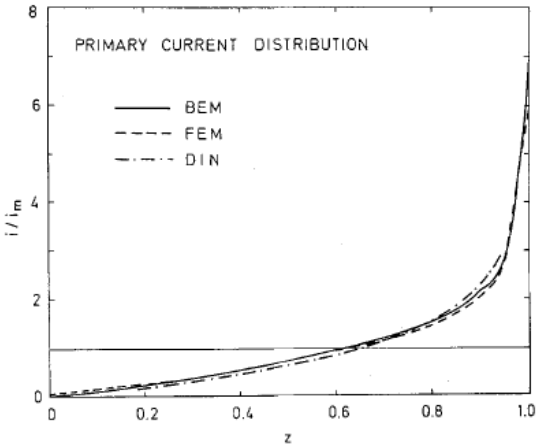


Fig. 3. Primary current distribution in the Hull cell calculated with the boundary element method (solid line), with the finite element method (dashed line), and with an empirical formula (broken line).

Please comment on the effect that moving the counter electrode farther away from the working electrode has on the primary and secondary current distributions. Also, name at least one advantage and one disadvantage of doing so.

For the primary distribution:

1D no effect on the current distribution, but the disadvantage is that ohmic losses are greater, bigger cell

2D/3D as the CE is moved farther away, the current distribution will become more uniform.

Secondary current distributions: assume that the characteristic length is the distance between electrodes. for Tafel kinetics

$$\mathrm{Wa} = \frac{RT}{FL} \cdot \frac{1}{i_{avg}\,\alpha_c}$$

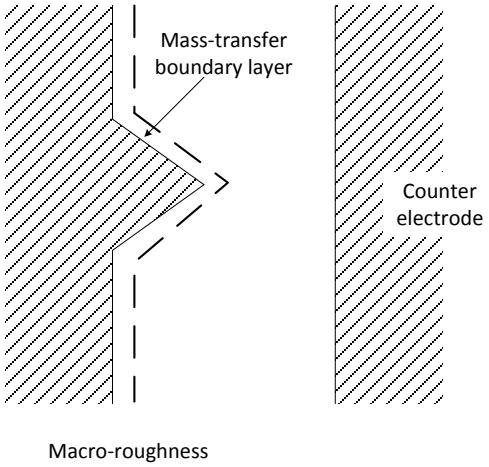
As the length, *L*, increases the Wa decreases and the current distribution becomes more uniform—it approaches the primary current distribution. The ohmic resistance increases but the kinetic resistance is unchanged.

Electro-polishing is an electrochemical process to improve the surface finish of a metal, whereby rough spots are removed anodically. Sometimes this leveling process is characterized as acting on *macro-roughness* or *micro-roughness*. Assume that there is a mass-transfer boundary layer on the surface.

a. Propose a mechanism for the leveling of macro-roughness, specifically where the thickness of the boundary layer is small compared to variations in the roughness.

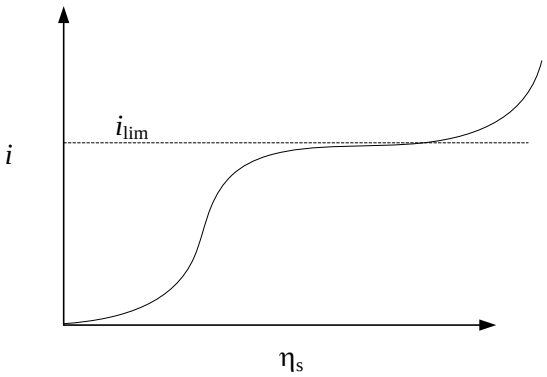
b. When silver is electro-polished in a cyanide bath, CN^- ions are needed at the surface to form $Ag(CN)_2^-$. Transport of the cyanide ion to the surface may limit the rate of dissolution of silver. Sketch how the current density for anodic dissolution of silver changes with the anode potential.

c. With micro roughness, the variation in thickness of the surface is less than that of the boundary layer. How would the diffusion of the cyanide ion to the surface affect the electro-polishing process?



a) Because the distance between the tip and the counter electrode is smaller than the nominal distance between the CE and the dissolving metal, the current density will be higher at the tip. This can be a result of higher rates of mass transfer (shorter diffusion path) or lower ohmic resistance (shorter conduction path). The rate of anodic dissolution is higher at the tip causing the surface to be leveled.

b) Normally metal dissolution would not be mass-transfer limited. However, when an acceptor ion (CN-) is needed the rate of dissolution of the metal can be limited by how fast the cyanide ion is transported to the electrode surface. The relationship between current density and overpotential would be the typical behavior for a mass-transfer limited condition.



c) The rate of mass transfer to the tip will be higher than over the flat portion of the electrode, thus the anodic current density will be higher and the metal will dissolve at a faster rate. see Wagner, *J. Electrochem. Soc.*, **101**, 225 (1954).

Derive equations 4-64 and 4-65.

$$\text{Wa} = \frac{R_{ct}}{R_\Omega} = \frac{\kappa}{L}\frac{d\eta}{di}$$

starting with Butler Volmer kinetics

$$i = i_o\left\{\exp^{\frac{\alpha_a F}{RT}\eta} - \exp^{\frac{-\alpha_c F}{RT}\eta}\right\}$$

we first restrict this to linear kinetics

$$i \approx i_o\left\{\frac{\alpha_a F}{RT}\eta + \frac{\alpha_c F}{RT}\eta\right\}$$

$$\frac{di}{d\eta} = \frac{i_o F}{RT}\{\alpha_a + \alpha_c\}$$

Therefore

$$\text{Wa} = \frac{\kappa}{L}\frac{d\eta}{di} = \frac{\kappa}{L}\frac{RT}{i_o F}\frac{1}{(\alpha_a + \alpha_c)}$$

For Tafel kinetics

$$i \approx -i_o\exp^{\frac{-\alpha_c F}{RT}\eta}$$

$$\frac{di}{d\eta} = \frac{\alpha_c F}{RT} i_o\exp^{\frac{-\alpha_c F}{RT}\eta}$$

We see that the derivative depends on the surface overpotential, η, which is not constant. Therefore, we replace $i_o\exp^{\frac{-\alpha_c F}{RT}\eta}$ with i_{avg}, the average current density.

$$\text{Wa} = \frac{\kappa}{L}\frac{RT}{F}\frac{1}{i_{\text{avg}}\alpha_c}$$

Suppose that you have an electrolysis tank that contains 10 pairs of electrodes. The tank is 75 cm long and the gap between electrodes is 4 cm. The tank is 26 cm wide, and the width of the electrodes is 20 cm. The distance between the electrodes and each side of the tank is 3 cm. The temperature is 25 °C.

The tank is used for the electrorefining of copper (i_o = 0.01 A·m^{-2}, α_a = 1.5, α_c = 0.5) at an average current density of 250 A·m^{-2}. The composition of the solution is 0.7 M $CuSO_4$ and 1 M H_2SO_4. The following properties are known:

$$D_{Cu^{2+}} = 0.72 \times 10^{-9} \text{ m}^2\text{s}^{-1}$$
$$D_{SO_4^{2-}} = 1.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$$
$$D_{H^+} = 9.3 \times 10^{-9} \text{ m}^2\text{s}^{-1}$$

Would you expect the secondary current distribution to be uniform or non-uniform? Please support your response quantitatively.

First, justify the use of Tafel kinetics

$$i = i_o \left\{ \exp^{\frac{\alpha_a F}{RT}\eta} - \exp^{\frac{-\alpha_c F}{RT}\eta} \right\}$$

Based on the current density provided and the kinetic data, the overpotentials are calculated.

at the anode $\eta_a = 0.17$ V

at the cathode $\eta_c = 0.52$ V

Both are greater than 100 mV, and therefore the Tafel approximation is good (Section 3.2.5)

Second, determine the solution conductivity from equation 4-7. The Nernst-Einstein relation (Eq. 4-27) is also used

$$\kappa = 103 \text{ S m}^{-1}$$

Next, calculate the Wa number

$$\text{Wa} = \text{Wa} = \frac{\kappa}{L}\frac{RT}{F}\frac{1}{\left|i_{\text{avg}}\alpha_c\right|}$$

The cathodic value is used because α_c is larger, which means it will be more non-uniform. The separation between the electrodes is used as the characteristic length, L=0.03 m

$$\text{Wa} = 0.53$$

This is an intermediate value, except near the edges the current distribution will be fairly uniform.

Use a charge balance on a differential control volume to show that $\nabla \cdot \boldsymbol{i} = 0$ at steady state.

$$\text{rate of accumulation} = \text{rate in} - \text{rate out}$$

There is not electron transfer reaction, so this equation does not include a generation term. Further, at steady state, the rate of accumulation is zero. Thus in=out.

Perform a balance over a differential volume $\Delta x \Delta y \Delta z$.

$$(i|_x - i|_{x+\Delta x})\Delta y \Delta z + \left(i|_y - i|_{y+\Delta y}\right)\Delta x \Delta z + (i|_z - i|_{z+\Delta z})\Delta x \Delta y = 0$$

divide by $\Delta x \Delta y \Delta z$, take the limit as Δ goes to zero.

$$\frac{\partial i_x}{\partial x} + \frac{\partial i_y}{\partial y} + \frac{\partial i_z}{\partial z} = 0 = \nabla \cdot \boldsymbol{i}$$

Permeation of vanadium across an ionomer separator of a redox-flow battery should be kept small for high efficiency. In contrast to a simple porous material, for an ionomer membrane separator there can be partitioning between the bulk solution and the ionomer membrane, see Figure 4-18. Consider the case when the current is zero.

a. If this equilibrium is represented by a partition coefficient, $K = \frac{c_i^{\text{membrane}}}{c_i^{\text{bulk}}}$, what is the expression for the molar flux across the separator analogous to Fick's law?
b. The product of solubility and diffusivity is called permeability, here equal to *DK*. For a permeability of 4×10^{-11} $m^2 \cdot s^{-1}$, estimate the steady-state flux of vanadium across a membrane that is 100 μm thick. On one side the concentration of V is 1 M, whereas on the other side assume the concentration is zero.
c. This flux results in a loss of current efficiency for the cell. If the valence state of vanadium changes by one, what current density does this flux represent?

a)

$$c_i^m = c_i^b K$$

apply Fick's law to the membrane

$$J_i = \frac{D\Delta c_i^m}{L} = \frac{(DK)\Delta c_i^b}{L}$$

b) the permeability is $DK = 4 \times 10^{-12}\ \text{m}^2\ \text{s}^{-1}$

$$J_i = \frac{(DK)\Delta c_i^b}{L} = \frac{(4 \times 10^{-12})1000}{0.0001} = 4 \times 10^{-5}\ \text{mol m}^{-2}\ \text{s}^{-1}$$

c)

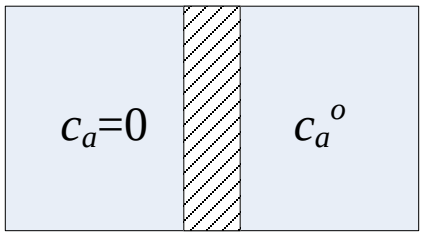
$$i = (4 \times 10^{-5})(1)F = 4\ \text{A m}^{-2}$$

It is possible to obtain both the diffusivity and the solubility of a diffusing species from one experiment. The experiment involves establishing the concentration on one side of the membrane and measuring the total amount of solute that is transported across the membrane as a function of time. Assume that at the start of the experiment, there is no solute in the membrane.

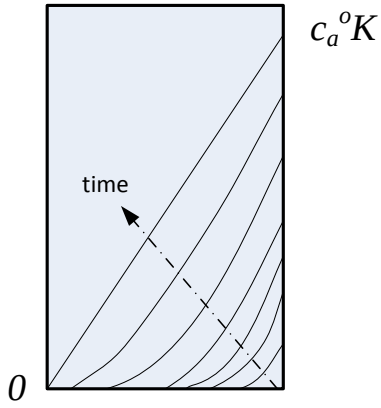
a. Sketch concentration across the membrane as a function of time. Your sketch should include the initial concentration, and the pseudo steady-state profile, *i.e.*, when the flux becomes constant.
b. Using the data provided, determined the permeability.

The time lag can be estimated, and the diffusivity calculated from the formula $\tau_{lag} = \frac{L^2}{6D}$. Using these data estimate both the diffusion coefficient and the partition coefficient for the solute. The concentration on one side is 1 M, and the thickness of the membrane is 400 μm.

Time, s	Total flux, $mol \cdot m^{-2}$.
45.9	0.0
90.0	0.0
136.9	0.0
179.3	0.5
226.0	1.1
270.9	2.8
315.8	4.4
359.0	6.7
403.5	9.4
446.6	11.9
489.6	14.7
536.9	17.7



a)

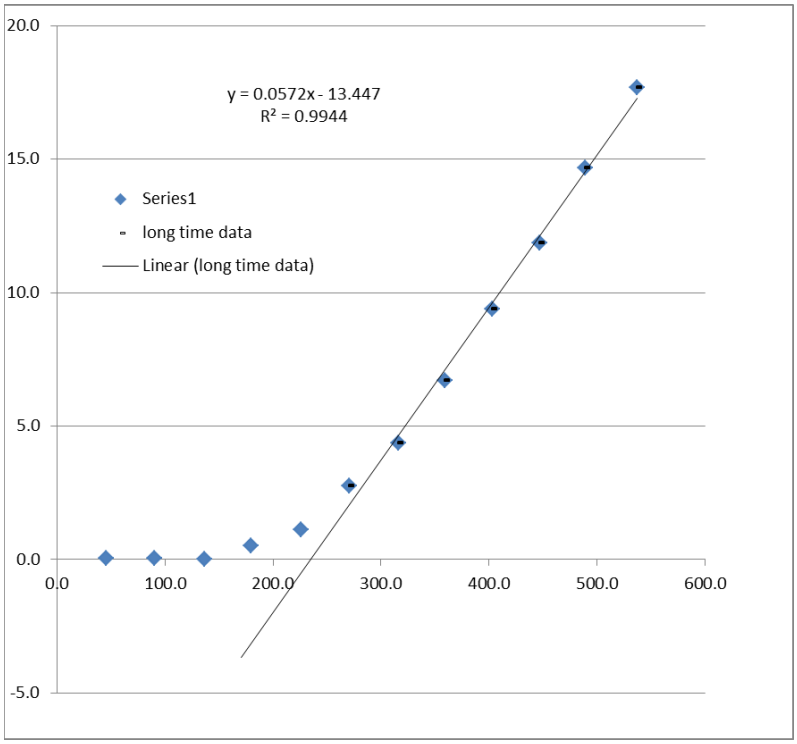


b)

$$J_i = \frac{(DK)\Delta c_i^b}{L}$$

$$DK = \frac{J_i L}{\Delta c_i^b} = \frac{(0.0572)(400 \times 10^{-6})}{1000} = 2.3 \times 10^{-8}\ \mathrm{m^2\ s^{-1}}$$

c) the data are plotted to determine the lag time



$$\tau_{lag} = 235 \text{ s}$$

apply Fick's law to the membrane

$$D = \frac{L^2}{6\tau_{lag}}$$

$$D = 1.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

$$DK = 2.3 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$$

$$K = \frac{2.3 \times 10^{-8}}{1.1 \times 10^{-10}} = 200$$

$$J_i = \frac{(DK)\Delta c_i^b}{L} = \frac{(4 \times 10^{-12})1000}{0.0001} = 4 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$$

c)

$$i = (4 \times 10^{-5})(1)F = 4 \text{ A m}^{-2}$$

The relative permeability of oxygen and hydrogen, $\alpha = \frac{\left(D/H\right)_{O_2}}{\left(D/H\right)_{H_2}}$, in a membrane is measured to be 0.4, where H_i is Henry's law constant representing the equilibrium between the gas phase and the ionomer defined in Equation 4-67. If air is on one side of the membrane and pure hydrogen on the other, both at atmospheric pressure, and the thickness of the membrane is L,

a. Estimate the relative rate of hydrogen permeation to of oxygen permeation across the membrane film
b. If there is a catalyst in the membrane where oxygen and hydrogen react instantaneously to form water, sketch the concentration of hydrogen and oxygen across the film.
c. Derive an expression that describes at what location in the membrane this reaction occurs? How will your answer change if the air is replaced with pure oxygen?

$$J_{O_2} = \left(D/H\right)_{O_2} \frac{p_{O_2} c}{L}$$

$$J_{H_2} = \left(D/H\right)_{H_2} \frac{p_{H_2} c}{L}$$

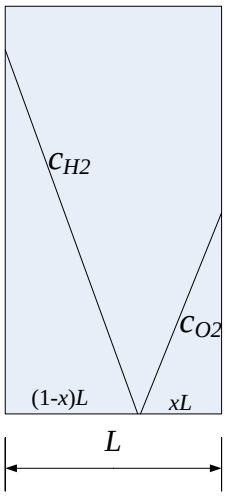
Finding the ratio of the two fluxes

$$\frac{J_{O_2}}{J_{H_2}} = \frac{\left(D/H\right)_{O_2}}{\left(D/H\right)_{H_2}} \frac{p_{O_2}}{p_{H_2}} = \frac{\alpha y_{O_2} p_{air}}{p_{H_2}}$$

$$p_{H_2} = p_{air}$$

$$\frac{J_{O_2}}{J_{H_2}} = \alpha y_{O_2}$$

b)



c) The reaction is

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

From this stoichiometry the magnitude of the hydrogen flux is twice that of oxygen. Thus,

$$\left(D/H\right)_{H_2} \frac{p_{H_2} c}{L(1-x)} = \left(D/H\right)_{O_2} \frac{p_{O_2} c}{Lx}$$

$$\frac{x}{1-x} = 2\frac{\left(D/H\right)_{O_2}}{\left(D/H\right)_{H_2}} \frac{p_{O_2}}{p_{H_2}} = 2\alpha \frac{p_{O_2}}{p_{H_2}}$$

$$\frac{1}{x} = 1 + \frac{1}{2\alpha} \frac{p_{O_2}}{p_{H_2}}$$

See *ESSL*, **10**, B101 (2007)

Calculate the Wagner number for the Zn and Ni electrodes discussed in Section 3.4, (i=4640 A m^{-2}). Comment on the values that you obtain and the relative magnitude of the kinetic and ohmic resistances that you calculated for this system. Are the values consistent with your expectations? Why or why not?

Ni $\alpha_a=\alpha_c=0.5$
Zn $\alpha_a=1.5$, $\alpha_c=0.5$ κ=60 S m^{-1}, L=2 mm

at i=4640 A m^{-2}, $\eta_s^{\mathrm{Ni}} = -0.2225$ V and $\eta_s^{\mathrm{Zn}} = 0.0627$ V

Use Tafel kinetics when calculating the Wa number

$$\mathrm{Wa} = \frac{RT\kappa}{FL}\frac{1}{i_{avg}\alpha}$$

For the Ni

$$\mathrm{Wa}^{\mathrm{Ni}} = \frac{RT(60)}{F(0.002)}\frac{1}{(4640)(0.5)} = 0.332$$

$$\mathrm{Wa}^{\mathrm{Zn}} = \frac{RT(60)}{F(0.002)}\frac{1}{(4640)(1.5)} = 0.111$$

These values indicate that the charge-transfer resistance is smaller than the ohmic resistance. The current distribution would not be uniform.

The discharge of the lead-acid battery proceeds through a dissolution/precipitation reaction. These two reactions for the negative electrode are

$$\mathrm{Pb} \rightarrow \mathrm{Pb}^{2+} + 2e^{-}, \qquad \text{dissolution}$$

and

$$\mathrm{Pb}^{2+} + \mathrm{SO}_4^{2-} \rightarrow \mathrm{PbSO}_4. \qquad \text{precipitation}$$

A key feature is that lead dissolves from one portion of the electrode but precipitates at another nearby spot. The solubility of Pb^{2+} is quite low, around 2 $g \cdot m^{-3}$. How then can high currents be achieved in the lead-acid battery?

a. Assume that the dissolution and precipitation locations are separated by a distance of 1mm with a planar geometry. Using a diffusivity of 10^{-9} m^2/s for the lead ions, estimate the maximum current that can be achieved.
b. Rather than two planar electrodes, imagine a porous electrode that is also 1mm thick with made from particles with a radius 10 μm packed together with a void volume of 0.5. What is the maximum superficial current here based on the pore diameter?
c. What do these results suggest about the distribution of precipitates in the electrodes?

a)

$$\boldsymbol{N}_{\mathrm{Pb}^{2+}} = D\frac{\Delta c}{L} = \frac{D}{L}\frac{\Delta \rho}{M}$$

$$i_{lim} = nF\boldsymbol{N}_{\mathrm{Pb}^{2+}} = nF\frac{D}{L}\frac{\Delta \rho}{M} = (2)(96485)\frac{10^{-9}}{10^{-3}}\frac{2}{207.2}$$

$$i_{lim} = 1.9 \times 10^{-3}\ \mathrm{A\ m^{-2}}$$

b) For a spherical particle

$$a = \frac{3(1-\varepsilon)}{r} = \frac{3(0.5)}{10^{-5}} = 1.5 \times 10^{5}\ \mathrm{m^{-1}}$$

$$I = aLnF\frac{D\Delta c}{2r} = 42\ \mathrm{A\ m^{-2}}$$

c) It is important that the current distribution be uniform through the thickness of the electrode to maximize the utilization of reactants. If the distribution were highly skewed to the front of the electrode, the pores may close, isolating the back of the electrode.

A porous electrode is made from solid material with an intrinsic density of ρ_s. When particles of this material are combined to form an electrode, it has an apparent density of ρ_a. What is the relationship between these two densities and the porosity? Assuming the particles are spherical with a diameter of 5.0 μm, what is the specific interfacial area? If the electrode made from particles with a density of 2,100 kg·m^{-3}is 1 mm thick and has an apparent density of 1,260 kg·m^{-3}, by what factor has the area increased compared to the superficial area?

a)

$$\rho_a = \frac{\text{mass}}{\text{total volume}} = \frac{\text{mass}}{V_{solid} + V_{void}}$$

$$\rho_a = \frac{\rho_s}{1 + \varepsilon/(1-\varepsilon)} = \rho_s(1-\varepsilon)$$

b)

$$a = \frac{6(1-\varepsilon)}{D} = \frac{6(1-0.4)}{5 \times 10^{-6}} = 7.2 \times 10^5 \text{ m}^{-1}$$

c) The surface area *A* is given by

$$A = A_s La$$

$$\frac{A}{A_s} = La = (10^{-3})7.2 \times 10^5 = 720$$

Calculate pressure required to force water through hydrophobic gas diffusion layer of PEM fuel cell. The contact angle is 140 degrees and the average pore diameter is 20 μm. Use 0.0627 [N/m] for the surface tension of water.

$$p_c = \frac{2\gamma \cos\theta}{r} = \frac{2(0.0627)\cos(140)}{2 \times 10^{-6}} = -4803 \text{ Pa}$$

the capillary pressure is the pressure of the non-wetting phase minus the pressure of the wetting phases

$$p_c = p_{\text{nw}} - p_{\text{w}}$$

Therefore, the pressure of the water is

$$(-) - 4803 \text{ Pa}$$

or 4803 Pa above the gas pressure.

The separator of a phosphoric acid fuel cell is comprised of micron and sub-micron sized particles of SiC. Capillary forces hold the liquid acid in the interstitial spaces between particles, and this matrix provides the barrier between hydrogen and oxygen. What differential gas pressure across the matrix can be withstood? Assume an average pore size of 1 μm, and use a surface tension of 70 $mN \cdot m^{-1}$, a contact angle of 10 degrees.

$$p_c = \frac{2\gamma \cos\theta}{r} = \frac{2(0.07)\cos(10)}{1 \times 10^{-6}} = 138 \text{ kPa}$$

The differential pressure (gas over liquid) must be greater than 138 kPa to force the gas across the separator.

The separator used in a commercial battery is a porous polymer film with a porosity of 0.39. A series of electrical resistance measurements are made with various numbers of separators filled with electrolyte stacked together. These data are shown in the table. The thickness of each film is 25 μm, the area $2x10^{-4}$ m^2, and the conductivity of the electrolyte is 0.78 S/m. Calculate the tortuosity. Why would it be beneficial to measure the resistances with increasing numbers of layers rather than just a single point?

Number of layers	Measured resistance, Ω
1	1.91
2	3.41
3	5.17
4	6.65
5	7.79

$$R_\Omega = \frac{nL}{A\kappa}\frac{\tau}{\varepsilon}$$

n	number of separator films
L	thickness of each film
κ	conductivity of the electrolyte
ε	porosity
τ	tortuosity
A	area

Plot the resistance versus the number of separator films, then fit line to the data. The slope is

$$\frac{dR_\Omega}{dn} = \frac{L}{\kappa A}\frac{\tau}{\varepsilon} = \text{slope}$$

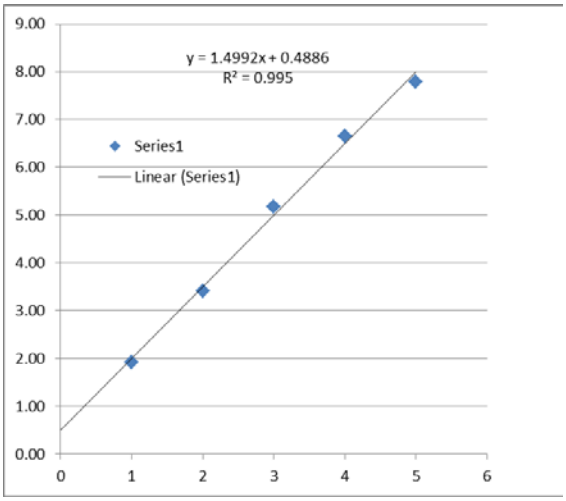
or

$$\tau = \text{slope}\frac{\kappa\varepsilon A}{L}$$

The slope is 1.4992, and therefore the tortuosity is 3.7.

$$\tau = 3.7$$

The resistance does not go to zero when n=0 because there is some additional resistance in series. This may be some contact resistance, but by using the slope of the line the effect is eliminated.



To reach the cathode of a proton exchange membrane fuel cell, oxygen must diffuse through a porous substrate. Normally, the porosity (volume fraction available for the gas) is 0.7 and the limiting current is 3000 $A \cdot m^{-2}$. However, liquid water is produced at the cathode with the reduction of oxygen. If this water is not removed efficiently, the pores can fill up with water, and the performance decreases dramatically. Use the Bruggeman relationship to estimate the change in limiting current when, because of the build-up of water, only 0.4, and 0.1 volume fraction are available for gas transport.

$$i_{\lim} = 3000\left(\frac{\varepsilon}{\varepsilon_o}\right)^{1.5}$$

ε=0.4 $i_{\lim} = 1300\ \text{A m}^{-2}$

ε=0.1 $i_{\lim} = 160\ \text{A m}^{-2}$

Calendering of an electrode is a finishing process used to smooth a surface and to ensure good contact between particles of active material. The electrode is passed under rollers at high pressures. If the initial thickness and porosity were 30 μm and 0.3, what is the new void fraction if the electrode is calendared to a thickness of 25 μm? What effect would this have on transport?

The mass of solids is unchanged

$$m_1 = m_2$$

$$\rho_1(1-\varepsilon_1)L_1A_1 = \rho_2(1-\varepsilon_2)L_2A_2$$

There is no change in area, and the solids don't compress, therefore

$$\varepsilon_2 = 1 - \frac{L_1}{L_2}(1-\varepsilon_1)$$

$$\varepsilon_2 = 1 - \frac{30}{25}(1-0.3) = 0.16$$

Electronic conductivity will likely get better because of better contact between particles. The effective conductivity and effective diffusion coefficient will be reduced because of lower porosity and a more tortuous path.

For a cell where σ>>κ, the reaction proceeds as a sharp front through the porous electrode. Material near the front of the electrode is consumed before the reaction proceeds toward the back of the electrode. This situation is shown in the figure, L_s is the thickness of the separator, L_e the thickness of the electrode, and x_r is the amount of reacted material.

a. If the cell is discharged at a constant rate, show how the distance x_r depends on time, porosity, and the capacity of the electrode, q, expressed in C/m^3.
b. What is the internal resistance? Use κ_s and κ for the effective conductivity of the separator and electrode respectively.
c. If the cell is ohmically limited, what is the potential during the discharge?

a) The current, I, is a constant.

$$\text{coulombs past} = iAt$$

The capacity of the electrode can also be expressed in coulombs. Let ε be the void fraction and q the capacity per volume

$$\text{coulombs past} = Ax_r(1-\varepsilon)q$$

$$iAt = Ax_r(1-\varepsilon)q$$

so

$$\boxed{x_r = \frac{it}{(1-\varepsilon)q}}$$

b)

$$\text{internal resistance} = \text{resistance of separator} + \text{resistance of electrodes}$$

$$R_{int} = \frac{L_s}{\kappa_s} + \frac{x_r}{\kappa}$$

substituting for x_r.

$$\boxed{R_{int} = \frac{L_s}{\kappa_s} + \frac{it}{(1-\varepsilon)q\kappa}}$$

c)

$$V = U - iR_{int} = U - i\left\{\frac{L_s}{\kappa_s} + \frac{x_r}{\kappa}\right\}$$

$$\boxed{V = U - i\left\{\frac{L_s}{\kappa_s} + \frac{it}{(1-\varepsilon)q\kappa}\right\}}$$

For Tafel kinetics and a one-dimensional geometry an analytic solution is also possible analogous to the one developed for linear kinetics. The solution is presented below for a cathodic process.

$$\frac{i_1}{I} = 2\theta \tan\left(\theta\frac{x}{L} - \psi\right),$$

and

$$\frac{di_1}{dx} = \frac{I}{L}\left\{\frac{2\theta^2}{\delta}\sec^2\left(\theta\frac{x}{L} - \psi\right)\right\},$$

where

$$\tan\theta = \frac{2\delta\theta}{4\theta^2 - \varepsilon(\delta - \varepsilon)} \qquad \tan\psi = \frac{\varepsilon}{2\theta}$$

$$\delta = \frac{\alpha_c FIL}{RT}\left(\frac{1}{\kappa} + \frac{1}{\sigma}\right) \qquad \varepsilon = \frac{\alpha_c FIL}{RT}\frac{1}{\kappa}$$

a. Make two plots of the dimensionless current distribution (derivative of i_1) for Tafel kinetics: one with K_r=0.1 and the second with K_r=1.0. δ is a parameter, use values of 1, 3, and 10.
Hint: it may be numerically easier to first find the value of θ that corresponds to the desired value for δ.

b. Compare and contrast the results in part (a) with Figure 5.6 and 5.7 for linear kinetics.

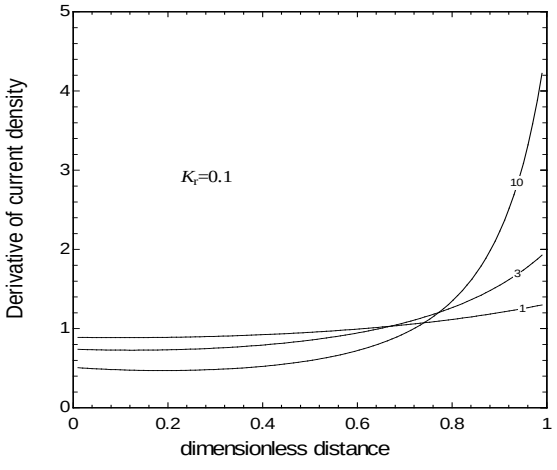
a) compare the above expressions for δ and ε

$$\delta\left(\frac{1}{\kappa} + \frac{1}{\sigma}\right)^{-1} = \varepsilon\,\kappa$$

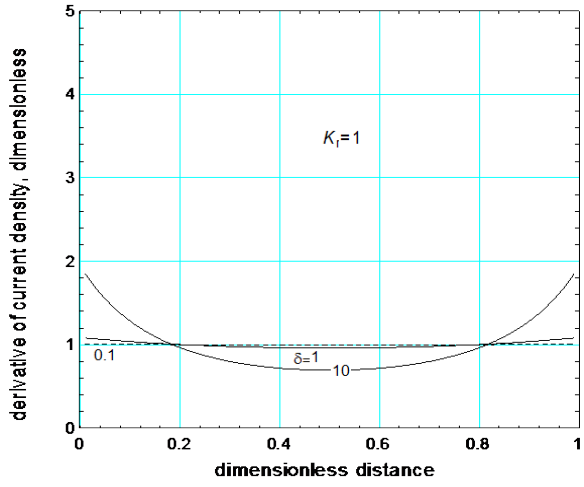
$$\delta = \left(1 + \frac{\kappa}{\sigma}\right)\varepsilon = (1 + K_r)\varepsilon$$

$$\tan\theta = \frac{2\delta\theta}{4\theta^2 - \varepsilon(\delta - \varepsilon)}$$

Find values of θ that correspond to the desired δ.



b)



The curves look very similar to those for linear kinetics, Figures 5.6 and 5.7. The parameter δ, which is proportional to I/A is replaced by ν^2, which is proportional to ai_o. For Tafel kinetics, the distribution becomes more non-uniform as the current is increased.

The two parameters that describe the current distribution in a porous electrode with linear kinetics in the absence of concentration gradients are

$$\nu^2 = \frac{ai_o(\alpha_a + \alpha_b)FL^2}{RT}\left(\frac{1}{\kappa}+\frac{1}{\sigma}\right) \qquad \text{and} \qquad K_r = \frac{\kappa}{\sigma}$$

a. How can the parameter ν^2 be described physically?

b. For the following conditions sketch out the current distribution $\frac{di_2}{dx}$ across the electrode

K_r=1	ν^2>>1
K_r =1	ν^2<<1
K_r =0.01	ν^2>>1

The parameter ν^2 is much like the Wagner number.

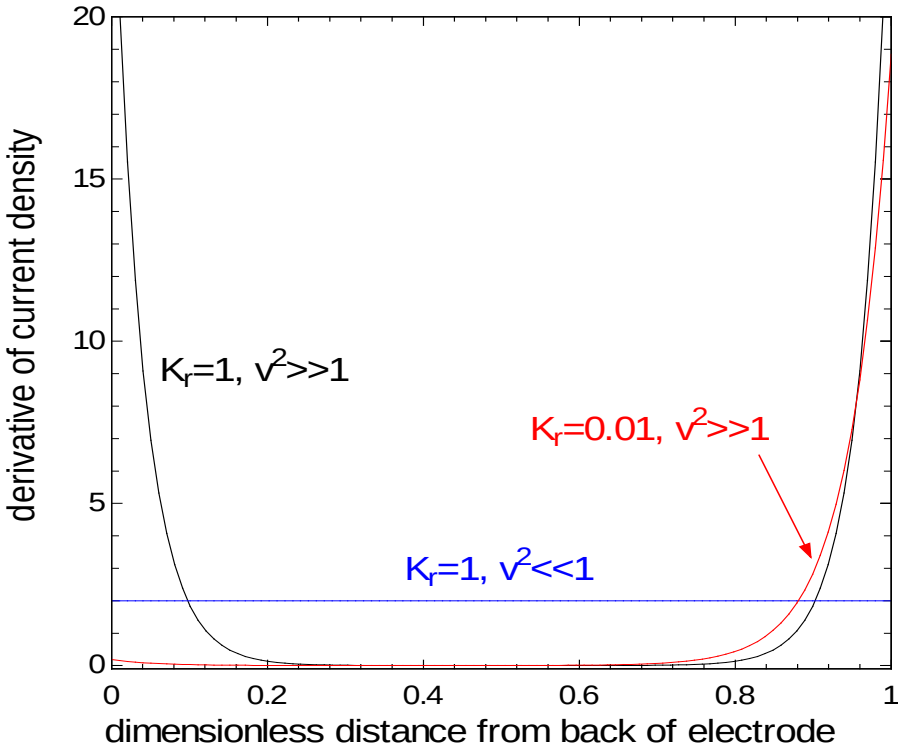
$$\nu^2 = \frac{ai_o(\alpha_a + \alpha_c)FL^2}{RT}\left(\frac{1}{\kappa}+\frac{1}{\sigma}\right)$$

$$\frac{1}{\mathrm{Wa}} = \frac{i_o(\alpha_a + \alpha_c)FL}{RT}\left(\frac{1}{\kappa}\right)$$

$$\nu^2 = \frac{\text{ohmic resistance}}{\text{kinetic resistance}}$$

large values of ν^2 correspond to small Wa, which leads to a non-uniform distribution

small values of ν^2 correspond to large Wa, which suggests a uniform distribution



Problem 5.9 provides the solution for the current distribution in a porous electrode with Tafel kinetics in the absence of concentration gradients. Describe the physical parameters? Compare and contrast these results to the analysis that lead to the Wa for Tafel kinetics found in Chapter 4.

Consider the cathodic case (the anodic situation is similar). There are two parameters

$$\varepsilon = \frac{\alpha_c F\left(I/A\right)L}{RT}\left(\frac{1}{\kappa}\right)$$

$$\delta = \frac{\alpha_c F\left(I/A\right)L}{RT}\left(\frac{1}{\kappa}+\frac{1}{\sigma}\right)$$

Compare these to the Wa, Equation 4-65.

$$\frac{1}{\mathrm{Wa}} = \frac{\alpha_c F\left|i_{\mathrm{avg}}\right|L}{RT}\left(\frac{1}{\kappa}\right)$$

By inspection δ is very similar to the reciprocal of the Wa.

$$\delta \propto \frac{\text{ohmic resistance}}{\text{kinetic resistance}}$$

small δ results in a uniform current distribution

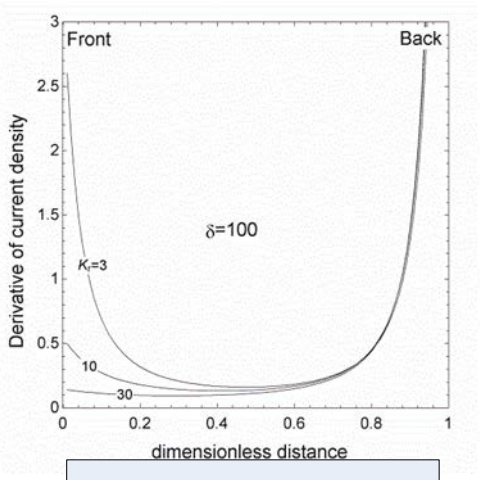
large δ results in a non-uniform distribution

Analysis of porous electrodes includes both the solution (1/κ) and the solid (1/σ) resistances, and thus a second parameter is needed. ε is used. If ε and δ are compared.

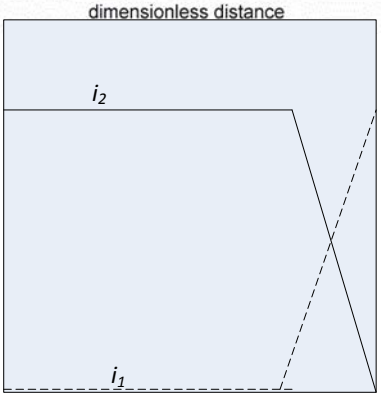
$$\delta = (1 + K_r)\varepsilon$$

where $K_r = \kappa/\sigma$. So either K_r or σ is the second parameter that affects whether the distribution is skewed to the front or to the back of the electrode, which is similar to the linear kinetics case.

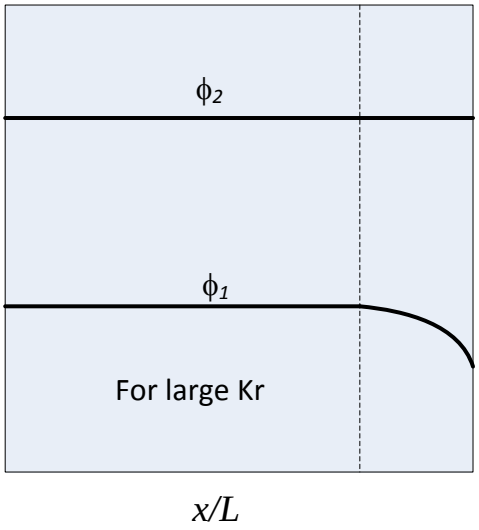
On the right is shown the current distribution in a porous electrode for Tafel kinetics. δ=100 and K_r is a parameter. As expected, for such a large value of δ, the current is highly non-uniform. Further, for the values of K_r chosen, the reaction is concentrated near the back of the electrode. Here, the scale of the ordinate has been selected to emphasize the behavior at the *front* of the electrode. Note, that in all cases rather than getting ever smaller at the front of the electrode, the derivative of current density always goes through a minimum and is increasing at the current collector. Physically explain this behavior.

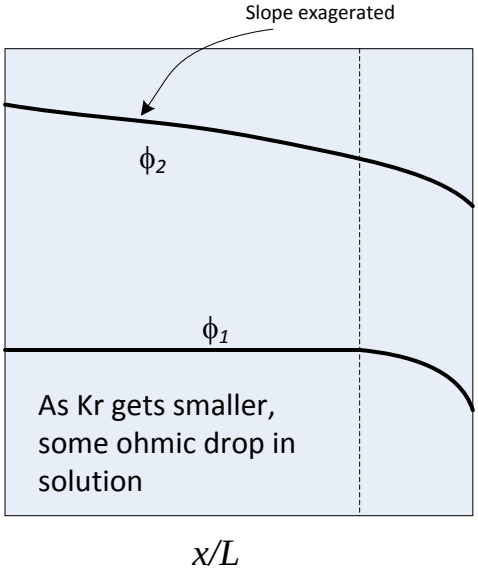


For large values of K_r, ($K_r = \kappa/\sigma$) the reaction is concentrated in the back of the electrode. As is shown in the figure, for a finite K_r the reaction rate always increases at the front of the electrode rather than going to zero. Further, the increase becomes larger as K_r gets smaller. This behavior can be understood by examining the solution and metal potentials (ϕ_1 and ϕ_2) across the electrode.



Start by assuming that all of the reaction is at the back of the electrode.





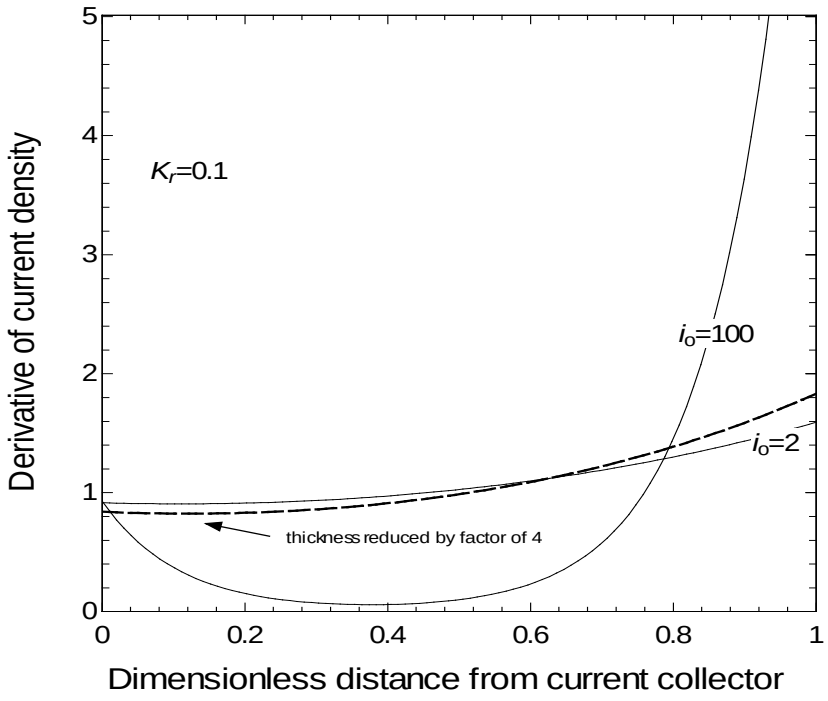
Because of the ohmic drop through the electrolyte, the potential at the front of the electrode increases as κ decreases,

$$\nabla \cdot \boldsymbol{i}_2 \propto \exp^{(\phi_2 - \phi_1)}$$

Thus, we see an exponential increase in current density in the front of the electrode.

An electrode is produced with a thickness of 1 mm, κ=10 S·m^{-1} and σ=100 S·m^{-1}. The reaction follows linear kinetics, i_o= 2 A·m^{-2} and the specific interfacial area is 10^4 m^{-1}. It is proposed to use the same electrode for a second reaction where the exchange current density is much larger, 100 A·m^{-2}. What would be the result of using this same electrode? What changes would you propose?

As produced the electrode has a relatively uniform current distribution. If the reaction has a higher exchange-current density, the current distribution becomes more non-uniform (see plot). In this case, the middle of the electrode is not being used.



Options to improve the current distribution are

- reduce *a*, use larger particles, which may be cheaper too.
- reduce the thickness of the electrode.

If the thickness is reduced by a factor of four, the current distribution approaches the original design.

The exchange current density i_o does not appear in the solution for the current distribution for Tafel kinetics (see how ε is defined in problem 9). Why not?

The situation is analogous to the Wa for Tafel kinetics described in Chapter 4.

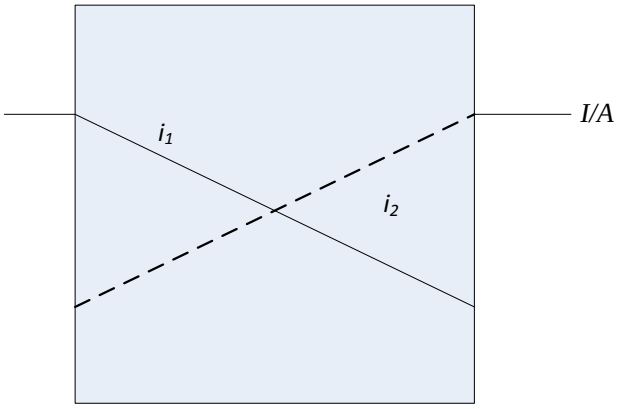
$$\frac{1}{\mathrm{Wa}} = \frac{\alpha_c F \left| i_{\mathrm{avg}} \right| L}{RT\kappa}$$

$$\varepsilon = \frac{\alpha_c F \left({}^{I}/_{A} \right) L}{RT\kappa}$$

Instead of the average current density, the superficial current density is used. With Tafel kinetics, the charge-transfer resistance decreases with increasing current. Whereas for linear kinetics it is proportional to $1/i_o$.

Rather than the profile shown in Figure 5-7, one might expect that for the case where σ=κ, that the distribution would be uniform and not just symmetric. Show that this cannot be correct. Start by assuming that the profile is uniform; then sketch how i_1 and i_2 vary across the electrode. Then sketch the potentials and identify the inconsistency.

Start by assuming that the current distribution is uniform.



$$i_2 = \frac{I}{A}\left(\frac{x}{L}\right)$$

$$i_1 = \frac{I}{A}\left(1 - \frac{x}{L}\right)$$

Applying Ohm's law

$$i_2 = -\kappa \frac{d\phi_2}{dx}$$

$$i_1 = -\sigma \frac{d\phi_1}{dx}$$

$$\int_0^{\phi_1(x)} d\phi_1 = -\frac{I/A}{\sigma}\int_0^x \left(1 - \frac{x}{L}\right) dx$$

$$\phi_1(x) = -\frac{I/A}{\sigma}\left(x - \frac{x^2}{2L}\right)$$

similarly

$$\phi_2(x) = \phi_2(0) - \frac{I/A}{\kappa}\frac{x^2}{2L}$$

$$\eta_s = \phi_1(x) - \phi_2(x) - U = \phi_2(0) - \frac{I/A}{\kappa}\frac{x^2}{2L}$$

if κ=σ

$$\eta_s = \left(I/A\right)\frac{1}{\sigma}\left(\frac{x^2}{2L} - x + \frac{x^2}{2L}\right) - \phi_2(0) - U$$

For the current distribution to be uniform, the surface over potential must be constant, we see however, that η_s is not a constant. Therefore our original assumption of a uniform current distribution is incorrect.

Repeat illustration 5-3 for a more conductive electrolyte, κ=100 S/m. If it is desired to keep the reaction rate at the back of the electrode no less than 40 % of the front, what is the maximum thickness of the electrode? Additional kinetic data are $\alpha_a = \alpha_c = 0.5$, $i_o = 100$ Am^{-2}, $a = 10^4$ m^{-1}. Using the thickness calculated, plot the current distribution for solutions with the following conductivities, 100, 10, 1, and 0.1 S/m.

Use equation 5-41

$$0.4 = \frac{1}{\cosh(\nu)}$$

solve for L from the definition for ν^2, Equation 5.31

$$\nu^2 \equiv \frac{a i_o (\alpha_a + \alpha_c) F L^2}{RT} \left(\frac{1}{\sigma} + \frac{1}{\kappa} \right) \qquad (5\text{-}31)$$

$$L = 2.5 \text{ mm}$$

Consider a similar problem to the flooded agglomerate model developed in Section 5.6, except that now a film of electrolyte covers the agglomerate to a depth of δ. Find the expression for the rate of oxygen transport that would replace equation 5-50.

Without the film present,

$$N_{O_2} = \frac{D_{eff} H p_{O_2}}{r_p}(1 - K\coth K)$$

With the film, let c_i be the oxygen concentration at the interface between the agglomerate and the film,

$$N_{O_2} = \frac{D_{eff} c_i}{r_p}(1 - K\coth K)$$

$$N_{O_2} = \frac{\left(H p_{O_2} - c_i\right)}{\delta} D_f$$

where D_f is the diffusivity of the film and δ the film thickness.

c_i is expressed as

$$c_i = \frac{N_{O_2} r_p}{D_{eff}(1 - K\coth K)}$$

which is substituted back into the film equation

$$N_{O_2} = \left[H p_{O_2} - \frac{N_{O_2} r_p}{D_{eff}(1 - K\coth K)}\right]\frac{D_f}{\delta}$$

or

$$N_{O_2} = \frac{H p_{O_2} \frac{D_f}{\delta}}{\frac{\delta}{D_f} + \frac{r_p}{D_{eff}(1 - K\coth K)}}$$

$$N_{O_2} = \frac{\frac{D_{eff}}{r_p}(1 - K\coth K) H p_{O_2}}{1 + \frac{\delta D_{eff}}{D_f r_p}(1 - K\coth K)}$$

Derive the expression for the effectiveness factor, equation 5-53. What is the expression for a slab rather than a sphere?

$$\eta = \frac{\text{actual reaction rate}}{\begin{array}{l}\text{reaction rate if entire particle}\\ \text{at O2 concentration at surface}\end{array}}$$

$$\eta = \frac{\left(4\pi r_p^2\right)\frac{Hp_{O_2}D_{eff}}{r_p}\left(K\coth K - 1\right)}{\left({}^4\!/_3\,\pi r_p^3\right)\left[K^2 Hp_{O_2}\,{}^{D_{eff}}\!/_{r_p^2}\right]}$$

$$\eta = \frac{3(K\coth K - 1)}{K^2}$$

A porous flow-through electrode was examined in Chapter 4 for the reduction of bromine in a Zn-Br battery.

$$Br_2 + 2e^- \rightarrow 2Br^-$$

The electrode is 0.1 m in length with a porosity of 0.55. What is the maximum superficial velocity that can be used on a 10 mM Br_2 solution if the exit concentration is limited to 0.1 mM? Use the following mass-transfer correlation.

$$\text{Sh} = 1.29\,\text{Re}^{0.72}$$

The Re is based on the diameter of the carbon particles, d_p and the superficial velocity, that make up the porous electrode.

$D_{Br_2} = 6.8\text{x}10^{-10}\ \text{m}^2/\text{s}$ $d_p = 40\ \mu\text{m}$ $\upsilon = 9.0\text{x}10^{-7}\ \text{m}^2/\text{s}$

$$c_L = c_{in}\exp(-\alpha L)$$

$$\alpha = \frac{ak_c}{\text{v}_x\varepsilon}$$

for a spherical particle, $a = \frac{6}{D_p}(1-\varepsilon) = 67{,}500\ \text{m}^{-1}$

$c_L = 0.1$ mM $c_{in} = 10$ mM

L is 0.1m, solve for alpha

$$\alpha = 46.05\ \text{m}^{-1}$$

then solve for the mass-transfer coefficient

$$k_c = 5.49 \times 10^{-5}\ \text{m s}^{-1}$$

$$\text{Sh} = 1.29\text{Re}^{0.72} = \frac{k_c D_p}{D_{Br_2}} = 3.23$$

$$\text{Re} = \frac{\varepsilon \text{v}_x D_p \rho}{\mu} = 3.575$$

$$\text{v}_s = \varepsilon \text{v}_x = 0.08\ \text{m s}^{-1}$$

Derive equation 5-42. Start with equation 5-36.

The resistance is defined as

$$R_{int} = \frac{\phi_1(L) - \phi_2(0)}{I/A}$$

$$i^* = \frac{K_r}{1+K_r} + \frac{\sinh(\nu z)+K_r\sinh(\nu(z-1))}{(1+K_r)\sinh(\nu)}. \quad (5\text{-}36)$$

y=x/L, a dimensionless distance
We can write Equation 5-36 as

$$i_2 = \frac{(I/A)\kappa}{\sigma+\kappa}\left\{1 + \frac{\sigma/\kappa\sinh(\nu(1-y))-\sinh(\nu y)}{\sinh(\nu)}\right\}.$$

also from Ohm's law

$$i_2 = -\kappa\frac{d\phi_2}{dx} = -\frac{\kappa}{L}\frac{d\phi_2}{dy}$$

$$\int_0^{\phi_2(1)} d\phi_2 = -\frac{(I/A)\kappa}{\sigma+\kappa}\frac{L}{\kappa}\int_0^1\left\{1 + \frac{\sigma/\kappa\sinh(\nu(1-y)) - \sinh(\nu y)}{\sinh(\nu)}\right\}dy$$

$$\phi_2(1) = -\frac{(I/A)L}{\sigma+\kappa}\left\{1 + \frac{1}{\nu\sinh(\nu)}\left[\sigma/\kappa\cosh(\nu-1) - \cosh(\nu) + 1\right]\right\}$$

For linear kinetics

$$\frac{di_1}{dx} = -\frac{ai_oF}{RT}(\alpha_a + \alpha_c)(\phi_1 - \phi_2)$$

Also, because charge is conserved

$$\frac{di_1}{dx} = -\frac{di_2}{dx}$$

$$\frac{-di_1}{dx} = -\frac{(I/A)}{L}\frac{\nu\kappa}{\sigma+\kappa}\{\sigma/\kappa\cosh(\nu(1-y)) + \cosh(\nu y)\}$$

since

$$\nu^2 = (\alpha_a + \alpha_c)\frac{ai_oF}{RT}L^2$$

$$\frac{-di_1}{dx} = \frac{\nu^2}{L^2}\left(\frac{1}{\kappa}+\frac{1}{\sigma}\right)^{-1}(\phi_1-\phi_2)$$

solve for $\phi_1 - \phi_2$ at *y*=1,

$$(\phi_1-\phi_2) = \frac{(I/A)L^2}{\nu^2}\left(\frac{1}{\kappa}+\frac{1}{\sigma}\right)^{-1}\frac{1}{L}\frac{\nu\kappa}{(\sigma+\kappa)}\frac{1}{\sinh(\nu)}\left[\frac{\sigma}{\kappa}+\cosh\nu\right]$$

$$\phi_1(y=1) = \frac{\left(\frac{I}{A}\right)L}{(\sigma+\kappa)}\left\{1+\frac{1}{\sinh(\nu)}\left[{}^{\sigma}/_{\kappa}\cosh(\nu-1)-\cosh(\nu)+1\right]\right\} - \frac{1}{\nu\sinh(\nu)}\frac{\left(\frac{I}{A}\right)L}{(\sigma+\kappa)}(1+{}^{\kappa}/_{\sigma})({}^{\sigma}/_{\kappa}+\cosh\nu)$$

$$R_{\text{int}} = \frac{L}{\sigma+\kappa}\left[1+\frac{2+\left(\frac{\sigma}{\kappa}+\frac{\kappa}{\sigma}\right)\cosh\nu}{\nu\sinh\nu}\right] \qquad (5\text{-}42)$$

Rearrange equation 5-57 to provide a *design equation* for a flow-through reactor operating at limiting current. Specifically, provide an explicit expression for *L*, the length of the reactor, in terms of flow rate, mass-transfer coefficient, and the desired separation

$$c_A = c_{A,in}\exp(-\alpha x)$$

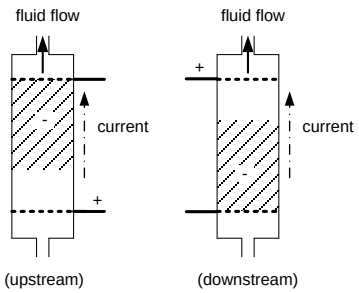
$$\alpha = \frac{ak_c}{\mathrm{v}_x\varepsilon}$$

$$\ln\frac{c_A}{c_{A,in}} = -\alpha x = \frac{ak_c}{\mathrm{v}_x\varepsilon}x$$

For length *L*, and $c_{A,o}$ the desired outlet concentration

$$L = \frac{\mathrm{v}_x\varepsilon}{ak_c}\ln\frac{c_{A,in}}{c_A} = \frac{\mathrm{v}_x\varepsilon}{ak_c}\ln(\text{separation factor})$$

A direct method of removing heavy metals, such as Ni^{2+}, from a waste stream is the electrochemical deposition of the metal on a particulate bed. The rate goal is to achieve as low concentration of Ni at the exit for as high a flow as possible. A flow-through configuration is proposed. However, here the negative electrode is porous, and the counter electrode (+) is a simple sheet. Would you recommend placing the counter electrode upstream downstream of the working electrode? Why? For this analysis assume only metal $\sigma >> \kappa$, and that the reaction at the electrode is mass-transfer limited. Hint: develop an expression for the change in solution potential similar to equation 5-63. and



If the reaction is mass-transfer limited, the concentration profile is the same regardless of where the counter electrode is places.

$$c_A = c_{A,in}\exp(-\alpha x)$$

The current density in solution is different

upstream, the current density is zero at $x=L$

$$i_2 = nF\mathrm{v}_x \varepsilon c_{A,in}\big(\exp(-\alpha x) - \exp(-\alpha L)\big)$$

downstream, the current density is zero at $x=0$

$$i_2 = nF\mathrm{v}_x \varepsilon c_{A,in}\big(1 - \exp(-\alpha x)\big)$$

Using Ohm's law

$$i_2 = -\kappa \frac{d\phi_2}{dx}$$

substitute for i_2 and integrate to find the potential difference

for the upstream placement, we get Equation 5.63

$$\Delta\phi_2 = \frac{nF(\mathrm{v}_x\varepsilon)^2 c_{A,in}}{K_{eff} a k_c} = \frac{\beta}{\alpha}$$

In contrast for downstream placement

$$\Delta\phi_2 = \beta\left[-L + \frac{1}{\alpha}(\exp(-\alpha L) - 1)\right]$$

For large L,

$$\Delta\phi_2 = -\beta L + \frac{\beta}{\alpha}$$

There is an additional term proportional to L. As we try to achieve higher separation by making the electrode larger, the potential difference increases. Thus, upstream placement is preferred.

You have been asked to measure the kinetics of nickel deposition from a Watts nickel plating bath. The conductivity of the plating solution is 3.5 S/m. The reference electrode is located 2 cm from the working electrode. The electrode area is 5 cm 2 (with only one side of the electrode active). You may neglect the impact of the concentration overpotential. You may also assume that the current density is nearly uniform.

a. Recommend a reference electrode for use in this system (hint- what is in the Watts bath?).

b. You apply a potential of 1.25 V and measure an average current density of 5 mA/cm 2 What is the surface overpotential? Is the IR drop in solution important? (assume a 1D uniform current density for this part).

c. How good is the assumption of uniform current density? What type of cell geometry would satisfy this assumption? How would your results be impacted if the current density were not uniform?

a. Watts Bath

Principal Components

1) Nickel Sulfate
2) Nickel Chloride
3) Boric Acid

Easiest to use a common reference electrode reversible to Cl^-

Use Ag/AgCl or SCE

b. Assume uniform current density between two electrodes that are $5cm^2$ in area.

$A = 5cm^2$

$L = 2cm =$ distance between ref. electrode and working electrode.

$\kappa = 3.5\ S/m$

$$R = \frac{L}{\kappa A} = \frac{2cm}{\left(3.4\frac{S}{m}\right)\left(\frac{m}{100cm}\right)5cm^2}$$

$$= 11.4\ \Omega$$

$$I = \left(\frac{5mA}{cm^2}\right)(5cm^2) = 24mA$$

Voltage loss between ref. and working.

$$\Delta V = IR = (0.025)(11.4) = 0.285V$$

Surface Overpotential =

$$\Delta V_{working-ref} - \Delta V_{\Omega} = 1.25 - 0.285$$

$$= 0.965V$$

c. 1-D assumption is not often accurate for experimental cells, due to geometry.

In other words, the primary current distribution is typically not uniform.

The current distribution can still be uniform if $Wa >> 1$ (see chap. 4)

A rectangular cell where the electrodes (working and counter) occupied the complete surfaces of two opposite faces would have a uniform current distribution.

For a non-uniform current distribution, the surface overpotential would vary across the electrode and the ohmic drop between the working and reference electrodes would depend on the exact position and not just the separation distance.

One of your lab colleagues is attempting to measure the kinetics of the following reaction

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O,$$

which is used in the cathode of vanadium-based redox flow batteries. To simplify things, he is making the measurement at constant current. He finds that the potential decreases slightly with time, followed by an abrupt decrease and substantial bubbling.

a. Qualitatively explain the observed behavior.
b. Given the following parameters, how long will the experiment proceed until the abrupt change in potential is observed? Assume that there is excess H^+ in solution, and that the electrode area is 2 cm^2.

$D_{VO_2^+} = 4\times10^{-10}$ m^2 s^{-1}
$c_{VO_2^+} = 25$ mM
$I = 1$ mA

Part (a) The observation is likely due to a drop in the surface concentration due to mass transfer limitations.

Part (b) Use the Sand Equation to determine the time required to reach the mass transfer limit

I	1	mA		
Area	2	cm^2		
n	1			
F	96485			
Di	4.00E-06	cm^2/s	4.00E-10	m^2/s
ci∞	0.025	M	25	mol/m^3
i	0.0005	A/cm^2	5	A/m^2

$$\frac{i\tau^{0.5}}{c_i^{\infty}} = \frac{nFD_i^{0.5}\sqrt{\pi}}{2}$$

t = 73.1 s

An estimate of the diffusivity can be obtained by stepping the potential so that the reaction is mass transfer limited as described in the chapter. From the following data for V^{2+} in acidic solution, please estimate the diffusivity. The reaction is as follows

$$V^{2+} \rightarrow V^{3+} + e^{-} \ .$$

The bulk concentration of $V^{2+}$is 0.01 M, and the area of the electrode is 1 cm^2.

t (s)	I (mA)
0.5	6.2
1.0	4.1
5.0	1.7
10.0	1.28
25.0	0.86
60.0	0.58
600	0.17
6000	0.052
10,000	0.043

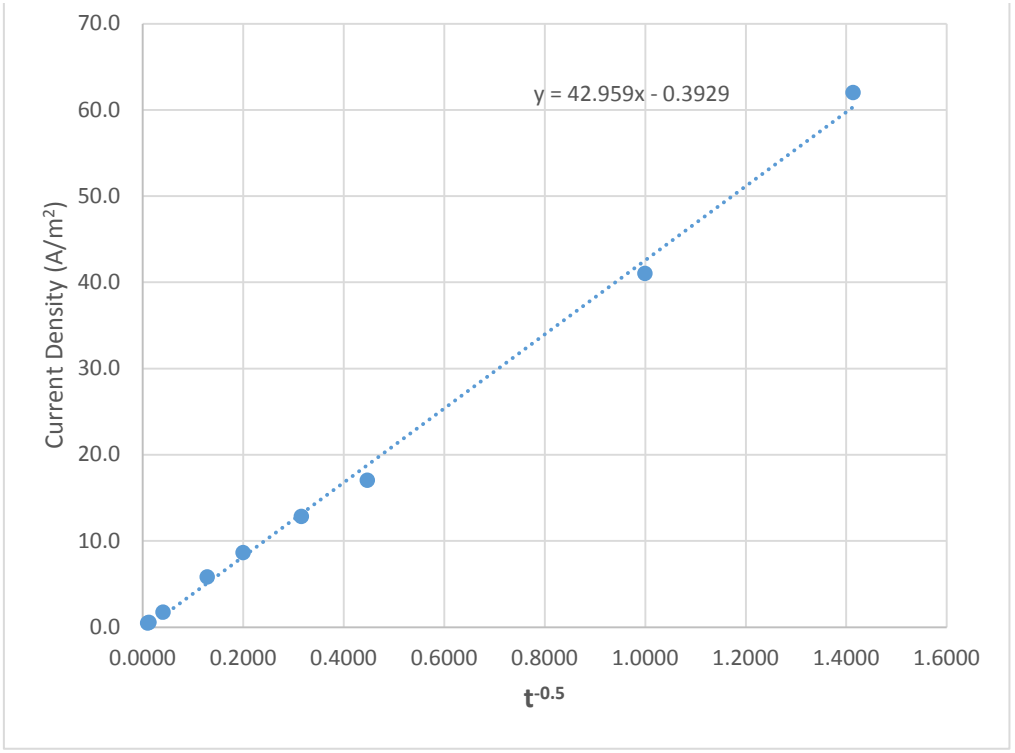
Area	1	cm^2	1.00E-04	m^2
n	1	eq/mol		
F	96485	C/eq		
c	0.05	M	50	mol/m^3

Based on the Cotrell Equation $$i = \frac{nF\sqrt{D_i}c_i^{\infty}}{\sqrt{\pi t}}$$

we can plot the current density as a function of 1/sqrt(t), and then solve for D from the slope

t (s)	1/sqrt t	I (mA)	i (A/m^2)
0.5	1.4142	6.2	62.0
1	1.0000	4.1	41.0
5	0.4472	1.7	17.0
10	0.3162	1.28	12.8
25	0.2000	0.86	8.6
60	0.1291	0.58	5.8
600	0.0408	0.17	1.7
6000	0.0129	0.052	0.5
10,000	0.0100	0.043	0.4

Slope	42.959
D_i	**2.49E-10**


y = 42.959x - 0.3929
Current Density (A/m²)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.0000
0.2000
0.4000
0.6000
0.8000
1.0000
1.2000
1.4000
1.6000
t-0.5

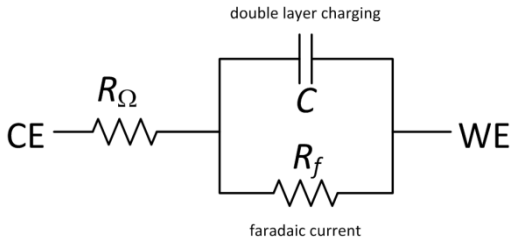
In section 6-4 we examined the time constant associated with charging of the double layer. In doing so, we assumed that the physical situation could be represented by a resistor (ohmic resistance of the solution) and a capacitor (the double layer) in series. However, the actual situation is a bit more complex since there is a faradaic resistance in parallel with the double layer capacitance as shown in Figures 6-6 and 6-24. This problem explores the impact of the faradaic resistance on double layer charging. Our objectives are two-fold: 1) determine the time constant for double layer charging in the presence of the faradaic resistance, and 2) determine an expression for the charge across the capacitor as a function of time.

a. Initially, there is no applied voltage, no current, and the capacitor is not charged

b. At time zero, a voltage V is applied

c. Your task is to derive an expression for the charge across the double layer as a function of time, and report the appropriate time constant. Use the symbols shown in Figure 6-17 for the circuit components.

Approach: The general approach is identical to that used in the chapter with the simpler model. In this case, you will need to write a voltage balance for each of the two legs, noting that the voltage drop must be the same. Remember that where "1" is the capacitor leg and "2" is the faradaic leg. Once you have written the required balances, you can combine them into a single ODE and solve that equation for the desired relationship and time constant. Finally, please explain physically how the characteristic time that you derived can be smaller than that determined for the simpler situation explored in the chapter.



$$V = const = IR_\Omega + \frac{Q}{C} \qquad (1)$$

$$= IR_\Omega + i_2 R_f \qquad (2)$$

$$I = i_1 + i_2$$

I is a function of t, as are i_1 and i_2

Express i_1 and i_2 in terms of Q_1 and Q_2

$$\frac{dQ}{dt}R_\Omega + \frac{Q_1}{C} = V \qquad (1)$$

$$\frac{dQ}{dt}R_\Omega + \frac{dQ_2}{dt}R_f = V \qquad (2)$$

$$\frac{dQ}{dt} = \frac{dQ_1}{dt} + \frac{dQ_2}{dt} \qquad (3)$$

$$\left(\frac{dQ_1}{dt} + \frac{dQ_2}{dt}\right)R_\Omega + \frac{dQ_2}{dt}R_f = V$$

$$\frac{dQ_1}{dt}R_\Omega + \left(R_\Omega + R_f\right)\frac{dQ_2}{dt} = V\mathrm{t}$$

$$\frac{dQ_2}{dt} = \frac{V - \frac{dQ_1}{dt}R_\Omega}{(R_\Omega + R_f)}$$

$$\frac{dQ_2}{dt} = \frac{V}{R_\Omega + R_f} - \frac{R_\Omega}{R_f + R_\Omega}\frac{dQ_1}{dt}$$

$$+\frac{Q_1}{C} = V$$

$$\frac{dQ_1}{dt}\left(R_\Omega - \frac{R_\Omega^2}{R_f + R_\Omega}\right) + \frac{Q_1}{C} = V\left(1 - \frac{1}{R_\Omega + R_f}\right)$$

$$\frac{dQ_1}{dt}\left(\frac{R_\Omega\left(R_\Omega + R_f\right) - R_\Omega^2}{R_\Omega + R_f}\right) + \frac{Q_1}{C} = V\left(1 - \frac{1}{R_\Omega + R_f}\right)$$

$$\frac{dQ_1}{dt}\left(\frac{R_\Omega R_f}{R_\Omega + R_f}\right) + \frac{Q1}{C} = V\left(1 - \frac{1}{R_f + R_\Omega}\right)$$

$$a\frac{dQ_1}{dt} + \frac{Q_1}{i} = b$$

$$a\frac{dQ_1}{dt} = b - \frac{Q_1}{C}$$

$$-C\left(\frac{-\frac{1}{C}dQ_1}{b - \frac{Q_1}{C}}\right) = \frac{1}{a}dt$$

$$\int_0^{Q_1} \frac{-\frac{1}{C}dQ_1}{b - \frac{Q_1}{C}} = -\frac{1}{aC}\int_0^t dt$$

$$\ln\left(b - \frac{Q_1}{C}\right)\Big|_0^{Q_1} = -\frac{1}{aC}t$$

$$\ln\left(b - \frac{Q_1}{C}\right) - \ln b = \frac{-1}{aC}t$$

Check limiting case

$$\left.\begin{matrix} b \to V \\ a \to R_\Omega \end{matrix}\right\} as\ R_f = \infty$$

$$\ln\left(1 - \frac{Q_1}{CV}\right) = \frac{-1}{RC}t$$

$\frac{Q}{Q_{final}} = 1 - exp^{-\frac{t}{RC}}$ (checks)

$$\ln\left(1 - \frac{Q_1}{bc}\right) = \frac{-1}{aC}t$$

$$b = V\left(1 - \frac{1}{R_\Omega + R_f}\right)$$

$$a = \frac{R_\Omega R_f}{R_\Omega + R_f}$$

$$\left(1 - \frac{Q_1}{bC}\right) = \exp\left(\frac{-t}{aC}\right)$$

This equation provides the charge in the capacitor "leg" as a function of a time starting from a zero charge condition. The time constant is $aC = \frac{R_\Omega R_f C}{R_\Omega + R_f}$

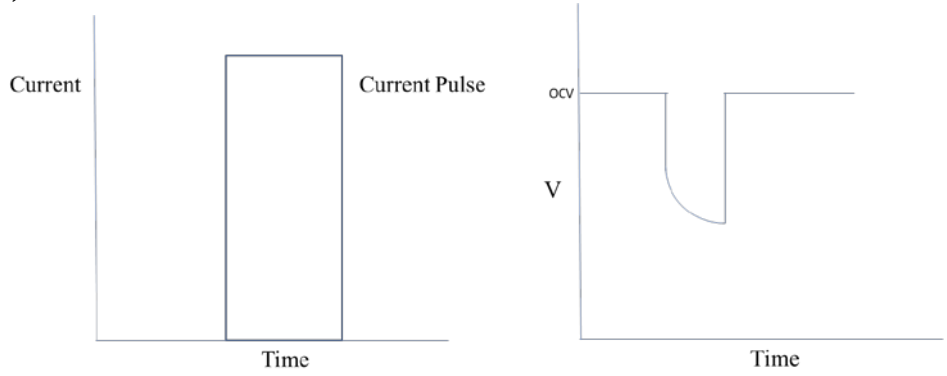
Time constant is smaller because full voltage does not have to be across the capacitor. In other words, the final current $\neq 0$ and the capacitor does not need to be charged to the same level.

GITT (Galvanostatic Intermittent Titration Technique) uses short current pulses to determine the diffusivity of solid phase species in, for example, battery electrodes where the rate of reaction is limited by diffusion in the solid phase. This situation occurs for several electrodes of commercial importance. The concept behind the method is to insert a known amount of material into the surface of the electrode (hence the short time), and then monitor the potential as it relaxes with time due to diffusion of the inserted species into the electrode. In order for the method to be accurate, the amount of material inserted into the solid must be known. For this reason, the method uses a galvanostatic pulse for a specified time, which permits determination of the amount of material with use of Faraday's Law assuming that all of the current is faradaic (due to the reaction).

a. While it is sometimes desirable to use very short current pulses, what factor limits accuracy for short pulses?
b. Assuming that you have a battery cathode, how does the voltage change during a current pulse?
c. For a current of 1mA and a 5cm^2 WE, what is the shortest pulse width (s) that you would recommend? Assume that you have a small battery cathode at open circuit, and that the drop in voltage associated with the pulse is 0.15 V. The voltage during the pulse can be assumed to be constant. The error associated with the pulse width should be no greater than 1%.

a) A key limiting factor is the time required for charging the double layer.

b)



c) $Q = I \cdot t = (0.001A)t$

$\Delta V = 0.15$ V as per problem statement

$Q = CV$ assume $C_{DL} = 0.2\ F/m^2$

$$Area = 5cm^2 = 0.0005\ \text{m}^2$$

$$C = C_{DL} \cdot A = 1x10^{-4}\text{F}$$

$$Q_{DL} = (1 \times 10^{-4}\text{F})(0.15\text{V})$$

$= 1.5 \times 10^{-5}$C (charge for DL)

Maximum Error $= 1\% = 0.01$

$$\frac{Q_{DL}}{Q_{total}} = 0.01 \qquad Q_{total} = 0.0015 \text{ C}$$

To get time,

$$Q_{total} = I \cdot t \qquad t = \frac{Q_{total}}{I}$$

$$t = \frac{0.0015\text{C}}{0.001} = 1.5\ s$$

Assumes:

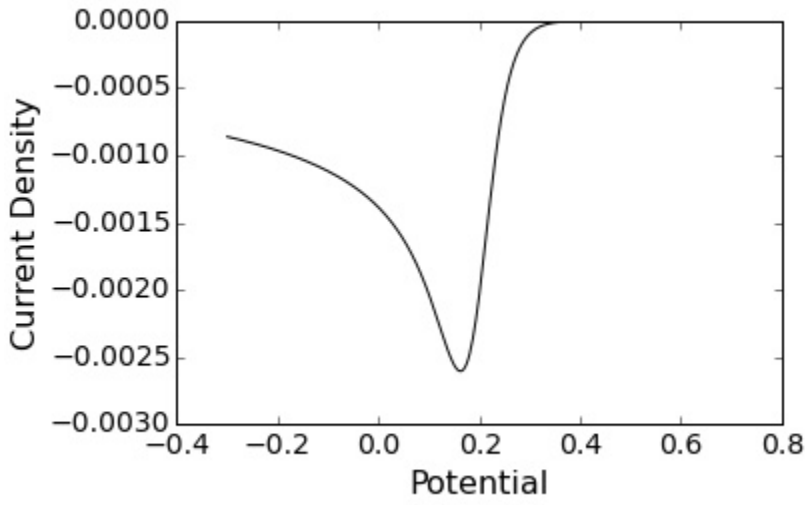
- Flat surface
- Constant capacitance
- Constant V in pulse

Note that C changes with electrode size.

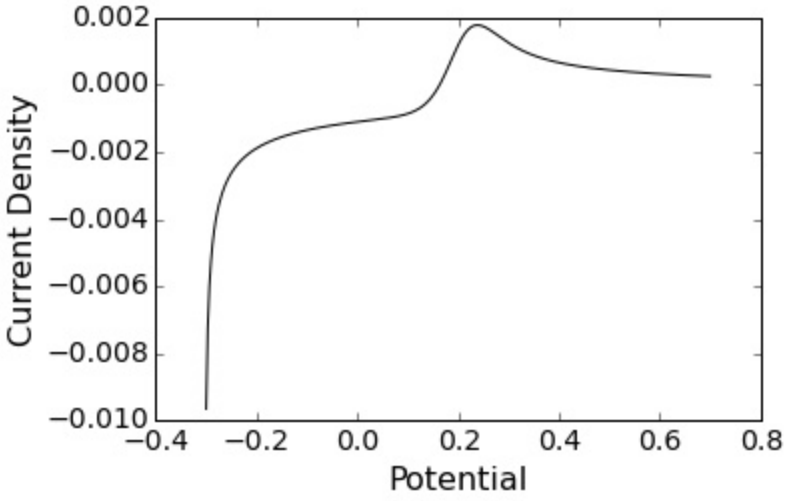
Assume that you have 50 mM of A^{2+} in solution, which can be reduced to form the soluble species A^{+}. Assume that the reaction is reversible with a standard potential of 0.2V. There is essentially no A^{+} in the starting solution. Please qualitatively sketch the following:

a. The IV curve that results from scanning the potential from a high value (0.5V above the standard potential of the reaction) to a low value (0.5V below the standard potential of the reaction).
b. The IV curve that results from scanning the potential from a low value (0.5V below the standard potential of the reaction) to a high value (0.5V above the standard potential of the reaction).
c. Why are the curves in (a) and (b) different?
d. Assuming that you started from the open circuit potential, in which direction would you recommend scanning first? Why?

a) (requests qualitative sketch) The actual curve for a sweep from 0.7 to -0.3V at 0.005 V/s as per simulation is



b) (requests qualitative sketch) The actual curve for a sweep from -0.3 to 0.7 V at 0.005 V/s as per simulation is



c) In (a), the scan starts in the oxidizing range at 0.7 V, and no current is observed initially since the reactant is already oxidized. Once the potential is sufficiently low, a cathodic current is observed, which peaks and then drops as typical for CV experiments.

In (b), the scan starts at -0.3V and a current is immediately observed due to reduction of the existing reactant. No peak is observed since both diffusion and the increasing potential lead to a reduction in the rate of the cathodic reaction. At positive potentials, a peak is observed as the reduced species near the electrode is oxidized.

d) Starting at the OCV, it makes sense to scan in the negative direction, since there are no reduced species in solution to react.

The following CV data were taken relative to a Ag/AgCl reference electrode located 1 cm from the working electrode. You suspect that the results may be impacted by IR losses in solution. The conductivity of the solution is 10 S/m.

a. Determine whether or not IR losses are important and, if needed, correct the data to account for IR losses.
b. Is it possible to determine n for the reaction from the data? If so, please report the value. If not, please explain why not.

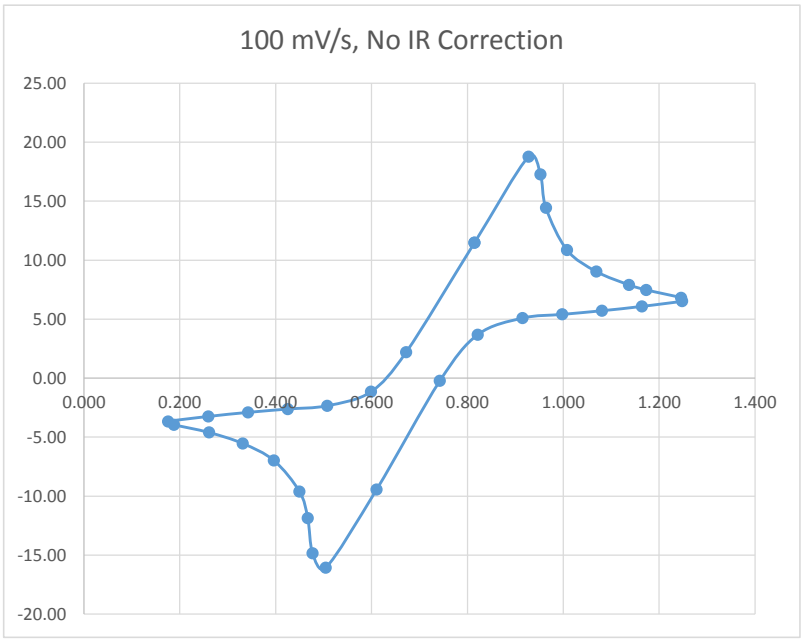
DV_{ir} iL/k

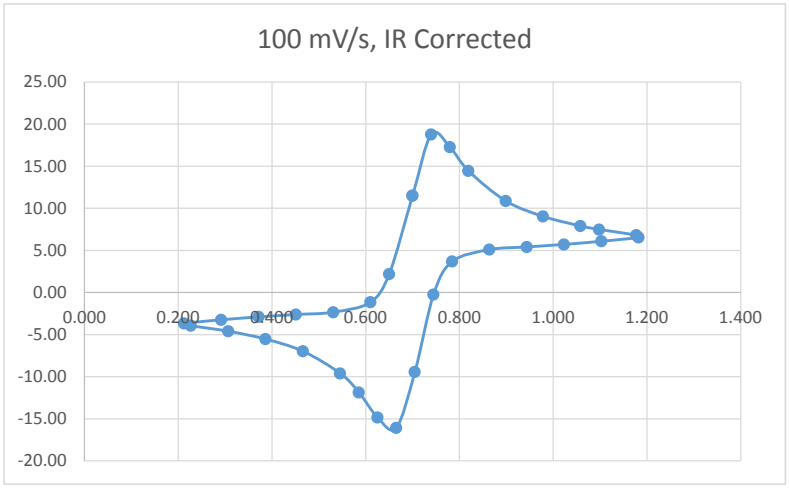
Data L 1 cm
k 0.1 S/cm

Do IR correction and compare plots. Start with 100 mV/s data

Scan Rate of 100 mV/s

Potential (V	V-iL/k	Current Density (mA/cm^2)
0.815	0.700	11.49
0.928	0.740	18.78
0.952	0.780	17.27
0.964	0.819	14.44
1.008	0.899	10.87
1.069	0.979	9.04
1.137	1.058	7.91
1.173	1.098	7.48
1.246	1.178	6.81
1.248	1.183	6.54
1.164	1.103	6.08
1.081	1.023	5.71
0.998	0.944	5.41
0.915	0.864	5.09
0.821	0.785	3.68
0.742	0.745	-0.23
0.611	0.705	-9.44
0.504	0.665	-16.08
0.477	0.625	-14.84
0.467	0.586	-11.87
0.450	0.546	-9.61
0.396	0.466	-6.98
0.331	0.387	-5.54
0.261	0.307	-4.61
0.188	0.227	-3.95
0.176	0.212	-3.68
0.260	0.292	-3.25
0.343	0.372	-2.90
0.425	0.451	-2.62
0.507	0.531	-2.34
0.599	0.610	-1.16
0.672	0.650	2.20
0.815	0.700	11.49

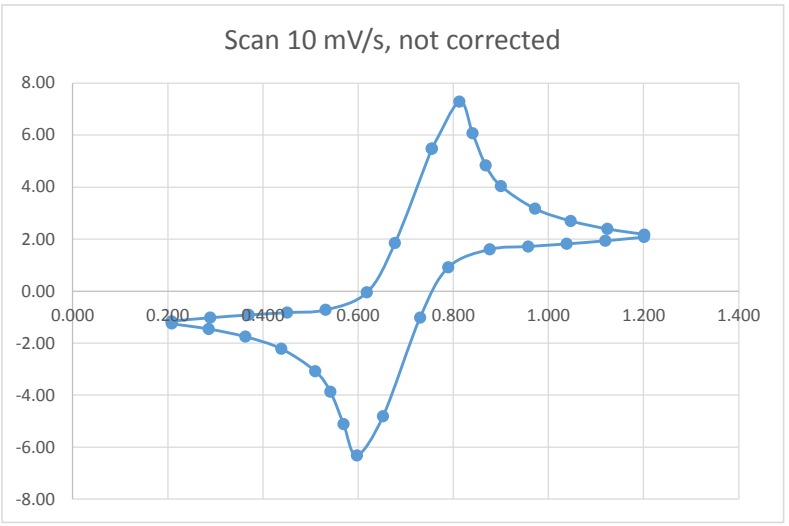


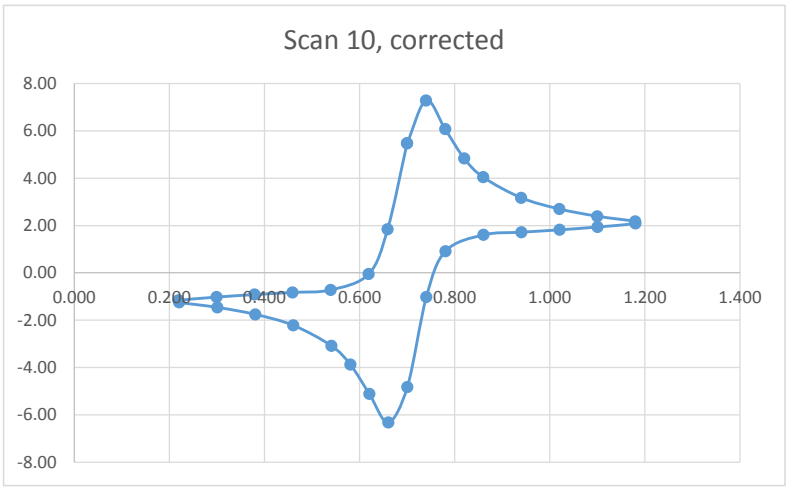


IR Correction makes a big difference. Need to compare corrected results to data at different scan rate to determine if reversible

Scan Rate of 10 mV/s

Potential (V	V-iL/k	Current Density (mA/cm^2)
0.755	0.700	5.48
0.813	0.740	7.28
0.841	0.780	6.07
0.868	0.820	4.83
0.900	0.860	4.04
0.972	0.940	3.17
1.047	1.020	2.70
1.124	1.100	2.39
1.201	1.180	2.17
1.201	1.180	2.08
1.120	1.100	1.94
1.039	1.020	1.82
0.958	0.940	1.72
0.876	0.860	1.60
0.790	0.780	0.91
0.730	0.740	-1.02
0.652	0.700	-4.82
0.597	0.661	-6.32
0.569	0.621	-5.11
0.542	0.581	-3.87
0.510	0.541	-3.08
0.438	0.461	-2.22
0.363	0.381	-1.75
0.286	0.301	-1.46
0.208	0.221	-1.25
0.208	0.219	-1.16
0.289	0.299	-1.02
0.370	0.379	-0.92
0.451	0.459	-0.82
0.532	0.539	-0.72
0.619	0.619	-0.05
0.677	0.659	1.85
0.755	0.700	5.48





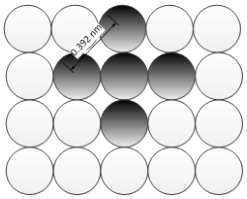
IR correction is important at both scan rates
The corrected data indicate that the peak positions are in the same place. Likely that the reaction is reversible.

(b) Since the system appears to be reversible, should be able to determine n
Data are limited, but we will see how it goes.

Peak to peak from 100 mV/s data

V positive peak	0.740
V negative peak	0.665
Difference	0.075

This is larger than the 60 mV expected for n=1, undoubtedly due to the limitations of the data.



For hydrogen adsorption on polycrystalline platinum, the accepted loading is 2.1 C/m^2. Using the (100) face shown in the diagram, calculate the amount of H adsorbed on this FCC surface assuming one H per Pt atom. Then, convert this number to the corresponding amount of charge per area. Assume a pure platinum surface with an FCC lattice parameter of 0.392 nm, and compare your results to the polycrystalline number. Provide a possible explanation for any differences between the calculated and accepted values.

First, we need to find the atoms per area. Based on the diagram above, the area is equal to 4a x 5a, where a is the diameter of a Pt atom. We can find the diameter of a Pt atom from the lattice parameter

$$a = \frac{0.392}{\sqrt{2}} = 0.277\ nm$$

Therefore, the area is 4a x 5a = 20a^2 = 1.537 nm^2=1.537 x 10^{-18} m^2

In this area, there are 20 Pt atoms.

$$\frac{20\ \text{atoms}}{1.537\cdot10^{-18}\,\text{m}^2}\left|\frac{\text{mol Pt}}{6.023\text{x}10^{23}\,\text{atoms}}\right|\frac{\text{mol CO}}{\text{mol Pt}}\left|\frac{2\ \text{equiv.}}{\text{mol CO}}\right|\frac{96485\ \text{C}}{\text{equiv.}} = 4.17\text{C m}^{-2}$$

This is the same number calculated in Section 6-6, and assumes that all the Pt sites are occupied. The accepted value is about half of this value, which implies that not all of the sites are occupied in practice, and/or that the single crystal density overestimates the number of sites where H can be absorbed.

The behavior of an inductor is described by the following differential equation

$$V = L\frac{dI}{dt}$$

where *L* is the inductance. Use this equation and the procedure illustrated in section 6-7 to derive an expression for the complex impedance, *Z*. Compare your answer to that found in Table 6-4.

The behavior of an inductor is described by the following differential equation

$$V = L\frac{dI}{dt}$$

where *L* is the inductance. Use this equation and the procedure illustrated in section 6-7 to derive an expression for the complex impedance, *Z*. Compare your answer to that found in Table 6-4.

$$V = L\frac{dI}{dt}$$

$$\mathcal{I} = \Delta I e^{j(\omega t - \emptyset)} \qquad \text{(Complex Current)}$$

$$\frac{d\mathcal{I}}{dt} = \mathrm{j}\omega\Delta I e^{j(\omega t - \emptyset)}$$

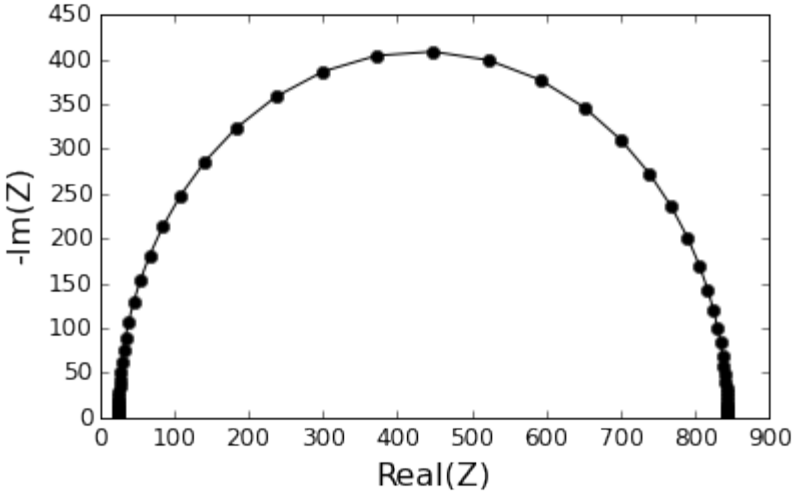
$$\mathcal{V} = L\frac{d\mathcal{I}}{dt} = Lj\omega\Delta I e^{j(\omega t - \emptyset)}$$

$$Z(\omega) = \frac{\mathcal{V}(\omega)}{\mathcal{I}(\omega)} = \frac{Lj\omega\Delta I e^{j(\omega t - \emptyset)}}{\Delta I e^{j(\omega t - \emptyset)}}$$

$$Z(\omega) = Lj\omega \qquad \text{same as Table 6-3}$$

Problem 6.10

In [14]:
```
from numpy             import *
from scipy.optimize    import *
from matplotlib.pyplot import *
%matplotlib inline

#input data
ro = 0.001                          #electrode radius m (1 mm)
R = 8.314;                          #Gas constant J/mol-K
T = 298;                            #Temperature K
F = 96485;                          #Faraday's Constant  C/mol
kappa=10;                           #conductivity S/m
cdl = 0.1;                          #specific capacitance F/m^2
inot = 10;                          #exchange current density A/m^2

Area = pi*ro**2.                    #electrode area m^2

C = cdl*Area                        #capacitance, F
Rohm = 1/(4.*kappa*ro)              #resistance to 1mm electrode (assumes
 other electrodes at infinity)

Rf = R*T/(F*inot*Area)              #kinetic resistance (linear kinetics,
 alphas add to 1)

def zcircuit(w):                   #w = frequency  rad/s
    zc = 1./(w*C*1j)               #impedance for capacitor
    zcir = Rohm+1./(1./(Rf)+1./zc); #calculate impedance for circuit  ohms
    return zcir;                   # return circuit impedance

w=logspace(-2,6,100);              #define frequency vector using log spa
cing because of large range of w
z=zcircuit(w);
x=z.real;
y=-z.imag;

plot(x,y,'k-o');
rc("font",size=12);
ax = gca()
xlabel(r'Real(Z)', size=16);
ylabel(r'-Im(Z)',size=16);

gcf().subplots_adjust(bottom=0.20);
savefig('ch6_6_3.jpg')
```


450
400
350
300
250
200
150
100
50
0
-Im(Z)
0
100
200
300
400
500
600
700
800
900
Real(Z)

In [14]:

In [ ]:

Please examine your response to previous problem and address the following

a. How does the magnitude of the kinetic and ohmic resistances compare to those calculated in Illustration 6-5? Please rationalize the differences and/or similarities.
b. How is it possible to use just the formula for the disk electrode to estimate the ohmic resistance? Do you expect this to be accurate? Why or why not?
c. In what ways does a large counter electrode influence the impedance results?

a. The property values in Illustration 6-5 and the previous problem are the same. The electrode sizes and geometry are different. From Illustration 6-5,

To determine the resistance of the electrolyte, we use equation 4-8c

$$\mathrm{R}_\Omega = \frac{L}{\kappa A} = \frac{0.01}{(10)(0.0025)} = 0.4\ \Omega$$

For the kinetic resistance, we assume open circuit as the steady-state condition, with small oscillations around that point. Because the magnitude of the potential change is small, linear kinetics can be used to determine the resistance according to equation 4-62

$$R_f = \frac{1}{A}\frac{d\eta}{di} = \frac{RT}{Fi_oA} = \frac{(8.314)(298)}{(96{,}485)(10)(0.0025)} = 1.03\ \Omega$$

The analogous values from Problem 6-8 are

$$\mathrm{R}_\Omega = \frac{1}{4\kappa r_o} = \frac{1}{4(10)(0.001)} = 25\ \Omega$$

$$R_f = \frac{1}{A}\frac{d\eta}{di} = \frac{RT}{Fi_oA} = \frac{(8.314)(298)}{(96{,}485)(10)\pi(0.001)^2} = 817\ \Omega$$

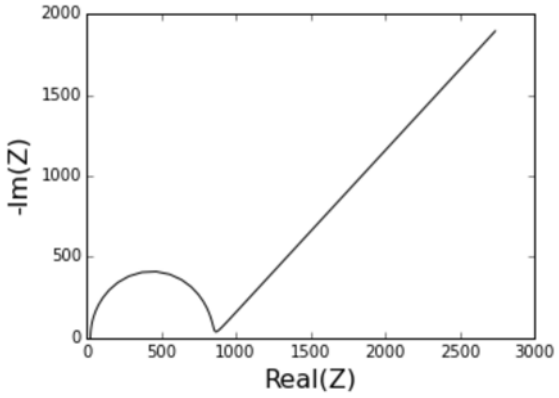
In both cases, the kinetic resistances are higher. However, the resistances for the microelectrode are much larger. Resistance relates the current (I) and the voltage (V), not the current density to the voltage. The resistances are much higher for the microelectrode because it is so much smaller and thus takes a much higher voltage to provide the same current (I).

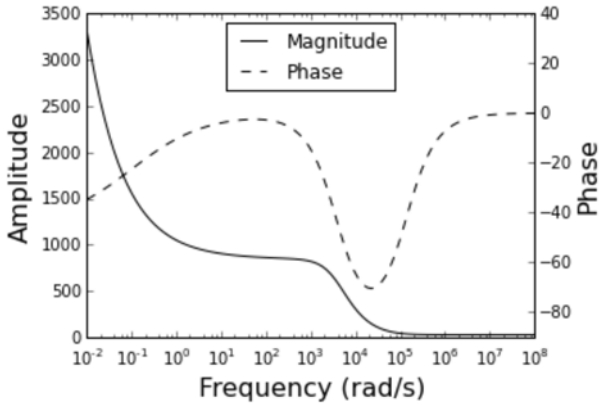
b. Essentially all of the ohmic loss occurs at the microelectrode (within 10-20 radii of the electrode). Therefore, the ohmic losses associated with that electrode essentially represent the total ohmic loss.

c. Use of a large counter electrode reduces its influence on the experiment by reducing kinetic losses ohmic losses and double layer capacitance effects. It is frequently a good idea to use a large counter electrode.

Problem 6.12

In [76]:
```
from numpy             import *
from scipy.optimize    import *
from matplotlib.pyplot import *
%matplotlib inline

#input data
np = 100                              #number of frequency points used (log
 spaced)
ro = 0.001                            #electrode radius m (1 mm)
R = 8.314;                            #Gas constant J/mol-K
T = 298;                              #Temperature K
F = 96485;                            #Faraday's Constant  C/mol
kappa=10;                             #conductivity S/m
cdl = 0.1;                            #specific capacitance F/m^2
inot = 10;                            #exchange current density A/m^2
D = 1.e-9;                            #diffusivity m^2/s
co = 10;                              #mol/m^3

Area = pi*ro**2.                      #electrode area m^2

C = cdl*Area                          #capacitance, F
Rohm = 1/(4.*kappa*ro)                #resistance to 1mm electrode (assumes
 other electrodes at infinity)

Rf = R*T/(F*inot*Area)                #kinetic resistance (linear kinetics,
 alphas add to 1)

def zcircuit(w):                     #w = frequency  rad/s
    zc = 1./(w*C*1j)                 #impedance for capacitor
    zw = R*T/(F**2*Area*D*co)*sqrt(D/(1j*w))   #warburg
    zcir = Rohm+1./(1./(Rf+zw)+1./zc); #calculate impedance for circuit  o
hms
    return zcir;                     # return circuit impedance

w=logspace(-2,8,np);                #define frequency vector using log spac
ing because of large range of w
z=zcircuit(w);
x=z.real;
y=-z.imag;
a=abs(z);
ar=-y/x
p=[None]*np
for i in range(0,np):
    p[i]=degrees(arctan(ar[i]));

#set up two plots
figure(figsize=(5,4))
plot(x,y,'k-');
rc("font",size=10);
ax = gca()
xlabel(r'Real(Z)', size=16);
ylabel(r'-Im(Z)',size=16);
gcf().subplots_adjust(bottom=0.20);
savefig('ch6_6_10_nyquist.jpg')

fig=figure(figsize=(5,4))
ax = fig.add_subplot(111)
lns1=ax.plot(w,a,'k-',label='Magnitude');
rc("font",size=10);
ax = gca()
ax.set_xscale('log')
xlabel(r'Frequency (rad/s)', size=16);
ylabel(r'Amplitude',size=16);
ax2 = ax.twinx()
lns2=ax2.plot(w,p,'k--',label='Phase');
ax2.set_ylabel(r'Phase',size=16)
ax2.set_ylim(-90, 40)
lns = lns1+lns2
labs = [l.get_label() for l in lns]
ax.legend(lns, labs, loc=9)
gcf().subplots_adjust(bottom=0.20);
savefig('ch6_6_10_bode.jpg')
```

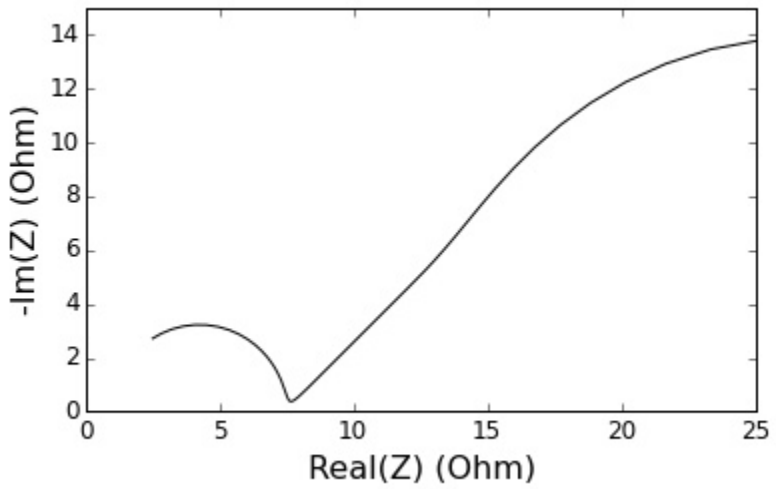

-Im(Z)
Real(Z)
0
500
1000
1500
2000
2500
3000


Magnitude
Phase
Amplitude
Phase
Frequency (rad/s)

In [ ]:

EIS data were taken for a system at the open circuit potential. Given the Nyquist diagram below,

a. Estimate the ohmic resistance
b. Estimate the kinetic resistance
c. Is it likely that the experimental system included convection? Why or why not?



a) Ohmic resistance can be estimated by "completing" the semicircle at the left side of the diagram. The value is approximately 1 ohm.
b) By continuing the semicircle on the right side, the sum of the kinetic and ohmic resistances is approximately 7.5 Ohm. Therefore, the kinetic resistance is 6.5 Ohm.
c) The diagram on the low frequency side does not continue linearly, but tapers off. This is reflective of a mass transfer layer with a finite thickness, and is likely the result of convection.

When measured about the open-circuit potential, the kinetic resistance is frequently larger than the ohmic resistance. However, for systems where mass transfer is not limiting, the ohmic drop inevitably controls at high current densities.

a. Given that the relative magnitude of the ohmic and kinetic resistance at high current densities has changed, is this because the ohmic resistance has increased or because the kinetic resistance has decreased? Please justify your response.
b. For the resistance that changed (kinetic or ohmic), please derive a relationship that describes how that resistance depends on the value of the current density.

a) The ohmic resistance stays constant. In other words, the ratio between the voltage drop in solution and the current density is a constant.

In contrast, the rate of the kinetic reaction is an exponential function of potential. Therefore, the apparent resistance decreases with increasing potential.

b) Assume Tafel Kinetics

$$i = i_o \exp\left(\frac{\propto_a F}{RT}(V-U)\right)$$

$$\frac{di}{dV} = \frac{i_o \propto_a F}{RT} \exp\left(\frac{\propto_a F}{RT}(V-U)\right)$$

$$\frac{di}{dV} = \frac{1}{A_{elec} R_\Omega} = \frac{\propto_a F}{RT} i$$

$$\therefore\ R_\Omega \propto \frac{1}{i}$$

The kinetic resistance is inversely proportional to the current, and therefore decreases with increasing current density.

The following data were taken with a RDE operating at the limiting current for a range of rotation speeds. The radius of the disk is 1 mm, and the reaction is a two-electron reaction. Assume a kinematic viscosity of 1.0×10^{-6} m^2 s^{-1}. The concentration of the limiting reactant is 25 mol m^{-3}. Please use a Levich plot to determine the diffusivity from the data given. Make sure that all quantities are in consistent units.

n	2	eq/mol				
F	96485	C/eq			Area	3.14159E-06 m2
r	1	mm	0.001	m		
v	1.00E-02	cm2/s	1.00E-06	m2/s		
c	25	mol/m3				

Speed (rpm)	sqrt omega	I (uA)	I (A/m2)
100	3.24	104	33.10
500	7.24	230	73.21
1000	10.23	325	103.45
1500	12.53	404	128.60
2000	14.47	470	149.61
2500	16.18	520	165.52
3000	17.72	565	179.85
3500	19.14	607	193.21
4000	20.47	660	210.08

Slope	10.207	
D^(2/3)	3.4125E-07	
D	1.9935E-10	m2/s

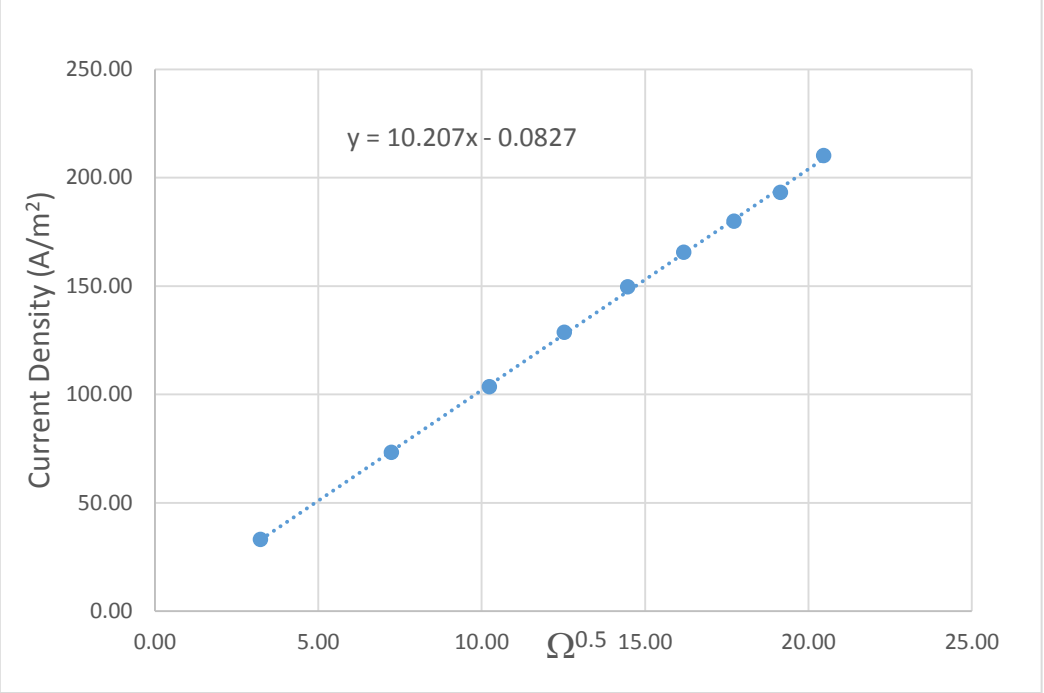


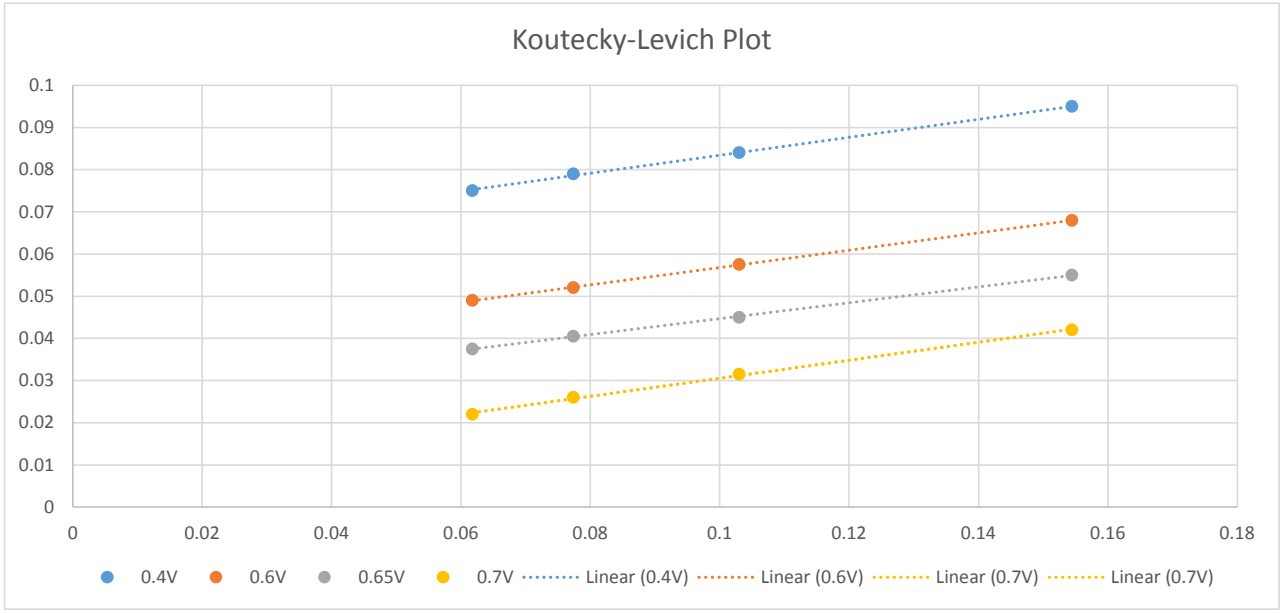
Illustration 6-6 is a Koutecký-Levich for oxygen reduction in water, where the bulk concentration is the solubility of oxygen in water as given in the problem. These data represent oxygen reduction in acid media, and the potential values given are relative to SHE. The equilibrium potential of oxygen is 1.23 V vs. SHE under the conditions of interest.

a. Using the data from the illustration, calculate the rate of reaction for oxygen at the bulk concentration at each value of the overpotential given in the illustration.

b. Determine the exchange-current density and Tafel slope assuming Tafel kinetics.

c. What assumption was made regarding the concentration dependence of i_o in the analysis above? Is the assumption accurate for oxygen reduction?

Rotation rate, rpm	Rotation rate, rad/s	$1/W^{0.5}$	i, A/m^2 0.7V	*1/i*	i, A/m^2 0.65V	*1/i*	i, A/m^2 0.6V	*1/i*	i, A/m^2 0.4V	*1/i*
2500	262	0.06178021	13.33	0.0750188	20.41	0.048996	26.67	0.03749531	45.45	0.022
1600	167	0.07738232	12.66	0.0789889	19.23	0.052002	24.69	0.04050223	38.46	0.026
900	94.2	0.10303257	11.9	0.0840336	17.39	0.057504	22.22	0.0450045	31.75	0.0315
400	41.9	0.15448737	10.53	0.0949668	14.71	0.067981	18.18	0.0550055	23.81	0.042
0	Intercept			0.0621703		0.036225		0.02581899		0.00921



				U	1.23	
Intercept data i vs. V				io	7.17E-01	Tafel Slope 0.377
f	h	i_intercept	i fit	error (normalized)		
0.4	-0.83	108.530241	114.06	-5.09E-02		
0.6	-0.63	38.7311838	33.62	1.32E-01		
0.65	-0.58	27.6055235	24.77	1.03E-01		
0.7	-0.53	16.0848593	18.25	-1.35E-01		
				4.87E-02	sumsqerror	

Analysis assumes that the concentration dependence is first order. This is not necessarily correct.

Suppose that you have a disk-shaped microelectrode that is 100 μm in diameter. At what value of time would the electrode be within 1 % of its steady-state current density? At what value of time would the electrode be within 10 % of its steady-state current density? What is the value of the limiting current at steady state in amperes? Assume a two-electron reaction with a diffusivity of 1×10^{-9} m^2 s^{-1} and a bulk concentration of 25 mM.

d	100	um	
n	2	eq/mol	
F	96485	C/eq	
D	1.00E-09	m2/s	
Cb	25	mM	mol/m3
a	0.00005	m	

$$i(t) = \frac{4nFD_i c_i^{\infty}}{\pi a} + \frac{\frac{8}{\pi^2} nFD_i^{0.5} c_i^{\infty}}{\sqrt{\pi t}}$$

Steady-state current

i	122.8	A/m2	Equation 6-68 (steady portion only)

Desire time (t) where the transient term in the equation is 1% of the steady-state value

$$\frac{\frac{8}{\pi^2} nFD_i^{0.5} c_i^{\infty}}{\sqrt{\pi t}}$$ = 0.01(steady-state current)

t	3225	s	
t	**53.8**	**minutes**	Time to 1% of steady state

t	32	s	
t	**0.54**	**minutes**	Time to 10% of steady state

I	= i*Area	
Area	7.85398E-09	m^2

I	**9.65E-07**	**A**	(just under a microamp)

You have been asked to design a disk-shaped microelectrode for use in kinetic measurements. You need to make measurements up to a maximum current density of 15 mA cm^{-2}. The concentration of the limiting reactant in the bulk is 50 mol m^{-3}, and its diffusivity is 1.2 $\times 10^{-9}$ m^2 s^{-1}. The conductivity of the solution is 10 S m^{-1}. Assume a single-electron reaction.

a. What size of microelectrode would you recommend? Please consider the impact of the limiting current and the uniformity of the current distribution.

b. What would the measured current be at the maximum current density for the recommended electrode?

Hint: Can you do kinetic measurements at the mass transfer limit? How does this affect your response to this problem?

a. The size of the electrode depends on how you decide to constrain the problem. For example, if you want to perform kinetic measurements up to a current density of 15 mA/cm2 at a surface concentration that does not change more than 10%, then you would need to operate at no more than 10% of the limiting current as per equation 6-70. Therefore,

$$\text{a.} \quad \frac{i}{i_{lim}} = 0.1 \qquad i_{ln} = \frac{15\frac{\text{mA}}{\text{cm}^2}}{.1} = 150\,\frac{\text{mA}}{\text{cm}^2}$$

$$a = \frac{4nFD_i c_i^{\infty}}{\pi i_{lim}} = 4.91 \times 10^{-6}\ \text{m}$$

radius ≈ 5 μm , diameter ≈ 10 μm

If, on the other hand, you are willing to account for the surface concentration and take measurements at different concentrations, you can take measurements up to the limiting current, although concentrations near the limiting current will be low and the tertiary current distribution will not be uniform for a disk electrode. At 90% of the limiting current

$$a = \frac{4nFD_i c_i^{\infty}}{\pi i_{lim}} = 4.42 \times 10^{-5}\text{m}$$

Radius ≈ 44 μm

Diameter ≈ 88 μm

Wa evaluates the uniformity of the secondary current distribution. To be conservative, we evaluate Wa for the largest electrode using the diameter as the characteristic length. For a current density of 15 mA/cm^2, assuming Tafel kinetics and an alpha value of 0.5 (see Chapter 4), the 88 micron electrode yields

$$Wa = \frac{RT\kappa}{diam\ F}\frac{1}{i_{avg}\alpha_c} \approx 400$$

This indicates that the secondary current distribution is nearly uniform.

b. The magnitude of the current is typically an issue of concern for microelectrodes. For the smaller electrode in (a) above,

$$I = i_{max}\pi r^2 = 1.14 \times 10^{-8}\text{A or about 10 nA}$$

This represents the maximum current, and is very small indicating one of the difficulties with use of an electrode close to 10 microns in diameter.

Derive an expression for the ratio of the iR drop associated with a microelectrode to that associated with a large electrode. Each of these two working electrodes (the microelectrode and the large electrode) is tested in a cell with the same current density at the electrode surface, and with the same reference electrode and counter electrode. Assume that any concentration effects can be neglected and that the current distribution is one-dimensional for the large electrode. Also assume that the distance L from the working electrode to the reference electrode is the same in both cases, and that L is large enough to be considered at infinity relative to the microelectrode.

Resistance for microelectrode disk

$$R_\Omega = \frac{1}{4\kappa a}$$

Where a is the disk radius. Assuming that the disk is sufficiently small so that the reference and counter electrodes are at infinity.

$$\Delta V_{microelectrode} = IR_\Omega$$

$$= iA_d R_\Omega$$

$$= \frac{iA_d}{4\kappa a}$$

For a large electrode located a distance L from the reference electrode.

$$R_\Omega = \frac{L}{\kappa A_L}$$

$$\Delta V_{large} = IR_\Omega$$

$$= \frac{iA_L L}{\kappa A_L} = \frac{iL}{\kappa}$$

$$\frac{\Delta V_{disk}}{\Delta V_{large}} = \frac{\frac{iA_d}{4\kappa a}}{\frac{iL}{\kappa}} = \frac{A_d}{4aL}$$

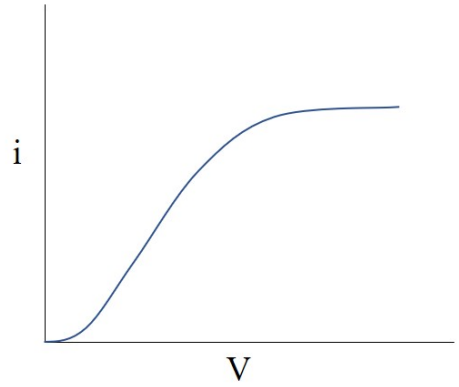
Given $A_d = \pi a^2$

$$\frac{\Delta V_{disk}}{\Delta V_{large}} = \frac{\pi a^2}{4aL} = \frac{\pi a}{4L}$$

The ΔV_{disk} at the same current density is much smaller. The ratio scales approximately as $\frac{a}{L}$

Qualitatively sketch the current response of a microelectrode to a slow voltage scan in the positive direction from the open-circuit potential. Assume that the solution contains an equal concentration of the reduced and oxidized species in solution. How does this response differ from that of a typically sized electrode? Please explain. Hint—What is the steady-state behavior of a microelectrode and how might this impact the shape of the CV curve?

There are two or three things about a microelectrode that make it different in a scan. The first is that the current will be much lower due to the small size of the electrode. Second, the current reaches a steady-state even under diffusion conditions (see Sec. 6-10). The third is that the time constant to reach steady-state is relatively fast. Because of these characteristics, the CV curve will reach a flat value, and show much less hysteresis on the return scan as the curve will tend to approach the steady-state value.



(Note- a fast scan may show a slight peak prior to flattening out.

However, it will still flatten out, while a large electrode continues to decline).

You need to measure the reduction kinetics of a reaction where the reactant is a soluble species. The reaction is a single electron reaction. The diffusivity is not known. As you answer the following, please include the equations that you would use and consider the implications of both mass transfer and the current distribution.

a. Can a rotating disk electrode be effectively used to make the desired measurements? If so, how would you proceed? If not, why not?
b. Is it possible to use a microelectrode to measure the quantities needed to determine the reduction kinetics? If so, how would you proceed? If not, why not?
c. What are the advantages and disadvantages of the two methods? Which would you recommend? Please justify your response.
d. What role, if any, does a supporting electrolyte play in the above experiments?

a. A rotating disk electrode can be used for the desired kinetic measurements provided that the range of current densities of interest is below the limiting current. The limiting current can be increased by changing the rotation rate. The procedure might be:
   1) Determine the diffusivity with use of experiments at the limiting current and different rotation rates. The current is related to the diffusivity by

$$i = 0.62nFD^{2/3}\Omega^{1/2}\nu^{-1/6}c^{\infty}$$

   and a Levich plot can be used to find D_i.

   2) Perform the kinetic measurements below the limiting current density. If the maximum current density at which a measurement is made is less than about 10% of the limiting current, then the bulk concentration can be used without introducing much error. Otherwise, the surface concentration needs to be determined as used as part of the analysis of the kinetics. The surface concentration can be estimated from

$$i = 0.62nFD^{2/3}\Omega^{1/2}\nu^{-1/6}(c^{\infty} - c_i)$$

   where c_i is the concentration at the surface.

   3) Note that although the mass transfer limited current is uniform with a rotating disk electrode, the secondary distribution is not necessarily uniform and may have an adverse impact on the accuracy of the results obtained. The uniformity of the secondary current distribution should be checked with use of Wa. Reduction of the disk size can improve uniformity.
   4) Depending on the length of the experiments and the container size, etc., one should make sure that the bulk concentration does not change appreciably during the experiment.

b. The same principles mentioned for the RDE also apply to a microelectrode.
    1) Measurements should be performed below the limiting current density, which can be estimated by

$$i_{lim} = \frac{4nF D_i c_i^{\infty}}{\pi a}$$

for a disk electrode, assuming that the transient time constant is fast for the small electrode.

    2) Perform the kinetic experiments below the limiting current density. In most cases, the limiting current density should be sufficiently high that the desired measurements can be made without the need to make a concentration correction. In needed, a correction for concentration can be made, although the concentration distribution at a disk electrode is not uniform.
    3) The secondary current distribution should be checked, but will likely be close to uniform for a very small electrode. Ideally, you should size your electrode so that this is so. Use the Wa number to guide you.

c. The microelectrode will generally permit measurements at higher current densities. The disadvantage of the microelectrode is the small magnitude of currents that must be measured accurately. The RDE system is also a bit more complex to operate.

d. The above measurements and analyses do not account for the impact of migration, which will influence transport in the absence of a supporting electrolyte. This may impact your experiments under certain conditions, but is not likely to be a significant factor in situations where kinetic limitations dominate. Still, you should check its impact in situations where a supporting electrolyte is not used.

A CV experiment is performed using a microelectrode with a diameter of 100 μm at room temperature. The potential is swept anodically at ν=10 mV/s. The double layer capacitance is 0.2 F/m^2. Recall that the charging current is $i_c = \nu C_{DL}$. The diffusivity of the electro-active species is 3×10^{-9} m^2/s. Assume that the fluid is stagnant. The concentration of the redox species is 100 mol/m^3 and the solution conductivity is 10 S/m. From the data for a sweep in the positive direction, determine the exchange-current density and the anodic transfer coefficient. The potentials are measured relative to a SCE reference electrode located far away from the microelectrode. The equilibrium potential of the reaction relative to SHE is 0.75V.

n	1			
D	3.00E-09	m2/s		
v	10	mV/s		
a	5.00E-05	m	50	mm
cbulk	100	mol/m3		
Cdl	0.2	F/m2		
K	10	S/m		
U	0.75	V	Hydrogen	
U	0.506	V	SCE	(assumes SCE at 0.244 V)

Data

V (SCE)	I (nA)
0.600	0.50
0.650	1.35
0.700	3.30
0.750	9.10
0.800	25.00
0.850	62.50
0.900	168.00
0.950	425.00
1.001	1200.00
1.052	3150.00
1.104	8000.00

Since we want kinetic data, want to be no more than about 10% of the mass transfer limit. This will give us kinetic values at the bulk concentration.

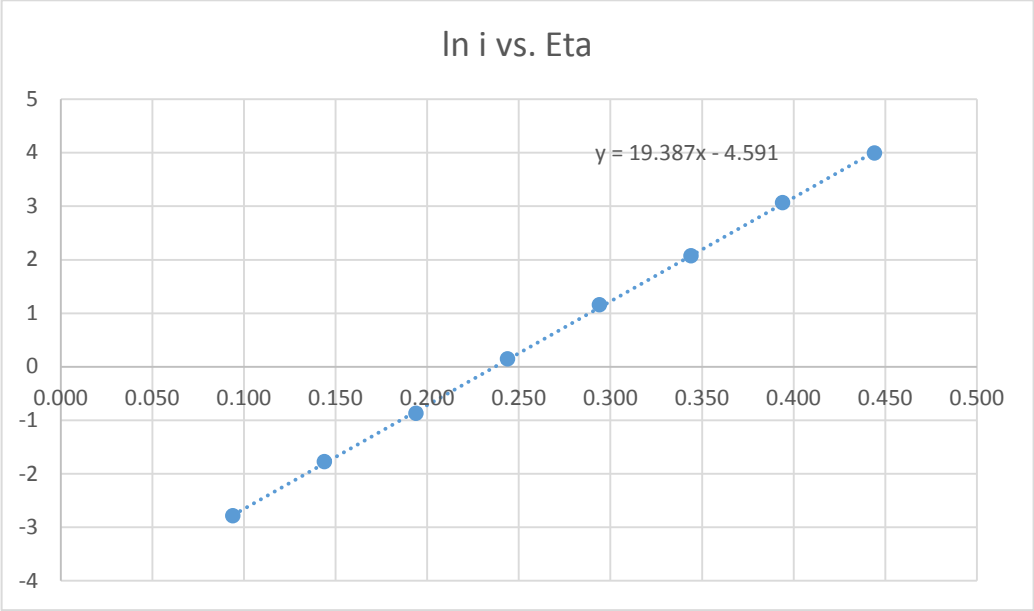
Calculate the mass transfer limit

i	737	A/m2	(current at mt limit- SS)

Use data in Tafel region to fit parameters

Equilibrium voltage is ~0.5, values should be > 0.6

V (SCE)	I (nA)	i (A/m2)	i (cap) A/m2	i (kinetic)	ln i	= IR = I/4Ka V(ohmic)	Eta
0.600	0.50	0.06	0.002	0.06	-2.7861	2.50E-07	0.094
0.650	1.35	0.17	0.002	0.17	-1.7726	6.75E-07	0.144
0.700	3.30	0.42	0.002	0.42	-0.8719	1.65E-06	0.194
0.750	9.10	1.16	0.002	1.16	0.14553	4.55E-06	0.244
0.800	25.00	3.18	0.002	3.18	1.15723	1.25E-05	0.294
0.850	62.50	7.96	0.002	7.96	2.07389	3.13E-05	0.344
0.900	168.00	21.39	0.002	21.39	3.06285	8.40E-05	0.394
0.950	425.00	54.11	0.002	54.11	3.99103	2.13E-04	0.444
1.001	1200.00	152.79	0.002	152.79	5.02904	6.00E-04	0.495
1.052	3150.00	401.07	0.002	401.07	5.99413	1.58E-03	0.546
1.104	8000.00	1018.59	0.002	1018.59	6.92617	4.00E-03	0.598
						Not significant	



Slope 19.38711
Intercept -4.591

a_a 0.498
i_o 0.010 A/m2

Given an elementary single-electron reaction described by the following kinetic expression

$$i\left[\frac{\mathrm{A}}{\mathrm{m}^2}\right] = 10.0\left(\frac{c_{ox,\mathrm{surf}}}{c_{ox,\mathrm{bulk}}}\right)^{0.5}\left(\frac{c_{red,\mathrm{surf}}}{c_{red,\mathrm{bulk}}}\right)^{0.5}\left[\exp\left(\frac{0.5F\eta_s}{RT}\right) - \exp\left(-\frac{0.5F\eta_s}{RT}\right)\right],$$

where the bulk concentration of each of the two reactants is 50 mM. You are to use a rotating disk electrode to measure the current density as a function of V for two different disk sizes, one with a 10 mm diameter, and a second with a diameter of 1 mm. *V* is measured against a SCE reference electrode located more than 5 cm from the disk, and the standard potential of the reaction is 0.1V SCE. Plot the *i* vs. *V* curve for each of the two electrodes for a range of current densities from -150 to 150 A/m^2 at a rotation speed of 500 rpm. Comment on any similarities and differences between the two curves. How does the size of the disk impact the mass transfer and the ohmic losses? You should account for the difference between the surface and bulk concentrations, including its impact on the equilibrium potential. Hint- it is easier to start with the current than it is with the voltage.

io	10	A/m2	W	500	rpm	52.3599 rad/s
credb	50	mol/m3	D	1.00E-09	m2/s	
coxb	50	mol/m3	n	1.00E-06	m2/s	
U	0.1	V				
k	10	S/m				

Add stoichiometry to problem statement

Yellow items need to be added to problem statement.

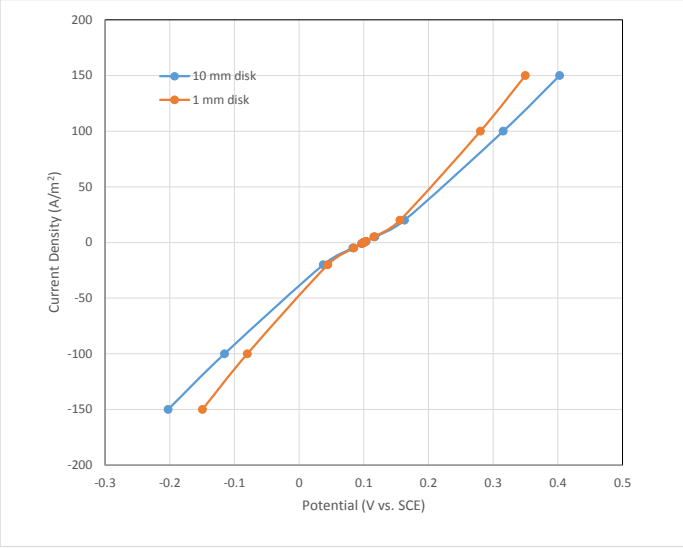
$$i = 0.62nFD_i^{2/3}\Omega^{1/2}\nu^{-1/6}\left(c^{\infty} - c_i\right)$$

$$R_{\Omega,disk} = \frac{V}{I} = \frac{1}{4\kappa a}$$

V = p i r_o/4k

formula to calculate ohmic drop in solution

i	coxsurf	credsurf	U	Vsurf	solver	10 mm di: V (ohmic)	1 mm disk V (ohmic)	Usurf - Ubul	10 mm V	1 mm V
150	84.65	15.35	0.14387	0.29987	-3.5929E-05	0.0589	0.00589	0.0438713	0.40265	0.34964
100	73.10	26.90	0.12569	0.2505	-2.72343E-05	0.03927	0.00393	0.0256862	0.31546	0.28012
20	54.62	45.38	0.10476	0.15018	4.87319E-06	0.00785	0.00079	0.0047617	0.1628	0.15573
5	51.16	48.84	0.10119	0.1139	-6.71241E-07	0.00196	0.0002	0.0011872	0.11705	0.11528
1	50.23	49.77	0.10024	0.1028	1.64577E-09	0.00039	3.9E-05	0.0002374	0.10343	0.10308
0.1	50.02	49.98	0.10002	0.10028	-2.09037E-09	3.9E-05	3.9E-06	2.374E-05	0.10034	0.10031
0	50.00	50.00	0.1	0.1	0	0	0	0	0.1	0.1
-0.1	49.98	50.02	0.09998	0.09972	-8.32158E-05	-4E-05	-4E-06	-2.374E-05	0.09966	0.09969
-1	49.77	50.23	0.09976	0.0972	2.01217E-12	-0.0004	-4E-05	-0.0002374	0.09657	0.09692
-5	48.84	51.16	0.09881	0.0861	3.58913E-12	-0.002	-0.0002	-0.0011872	0.08295	0.08472
-20	45.38	54.62	0.09524	0.04982	-1.04359E-05	-0.0079	-0.0008	-0.0047617	0.0372	0.04427
-100	26.90	73.10	0.07431	-0.0505	-1.48546E-05	-0.0393	-0.0039	-0.0256862	-0.1155	-0.0801
-150	15.35	84.65	0.05613	-0.0999	-2.05151E-05	-0.0589	-0.0059	-0.0438713	-0.2027	-0.1496



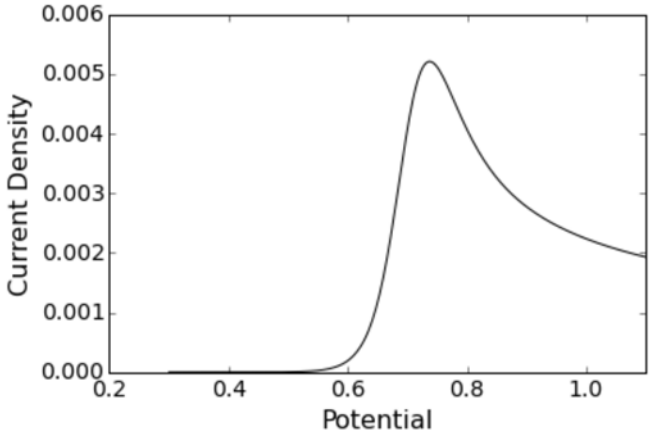
Notes

1) Start by specifying the current density, which simplifies the solution of the problem.
2) Once the current density is known, the surface concentration can be calculated with the RDE equation
3) With the current density and the surface concentration, the equilibrium potential at the surface and the applied voltage can be determined. I used the solver (line-by-line) to do this.
4) With the current density, the equation for the disk can be used to estimate the ohmic drop (do for both sized disks)
5) Calculate the difference in the equilibrium potential between the surface and the bulk
6) Can finally calculate the value of the "measured" potential and plot the requested i vs. V curves

Problem 6.24

In [8]:
```
from numpy             import *
from matplotlib.pyplot import *
from math              import *
%matplotlib inline

#constants
R = 8.314;                              #Gas constant J/mol-K
T = 298.15;                             #Temperature K
F = 96485;                              #Faraday's Constant  C/eq

#input data
Dox = 1.e-5                             #Diffusivity cm^2/s
Dred = 1.e-5                            #Diffusivity cm^2/s
L = 1.0;                                #Domain Length cm
Nx = 200                                # x grid points
cfl = 0.5                               # maximum value for stability
cox = 0.0                               #Initial concentrations (M)
cred = 0.100
neq = 1                                 #eq./mol for species of interest

Unot = 0.7
Estart = 0.3
Eend = 1.1
vscan = 0.005                           # V/s (use negative for negative scan
)
tend = (Eend-Estart)/vscan              # end time(s)

# define spatialgrid
x = linspace(0, L, Nx+1)                # mesh points in space
dx = x[1] - x[0]                        # calculate dx (evenly spaced)
# time step definition
D = min(Dox,Dred)                       #use minimum D for timestep calcs
dt = dx**2/D/2.*cfl                     # stable time step (half of maximum v
alue)
Nt = int(ceil(tend/dt));                # number of time steps
t = linspace(0, tend, Nt+1)             # mesh points in time

FFox = dt*Dox/dx**2                    #ratio of parameters for oxidation equ
ation
FFred = dt*Dred/dx**2                  #ratio of parameters for reduction equ
ation

#define and initialize (zero) arrays
u   = zeros(Nx+1)                       # unknown cox at new time level
u_1 = zeros(Nx+1)                       # cox at the previous time level
uu   = zeros(Nx+1)                      # unknown cred at new time level
uu_1 = zeros(Nx+1)                      # cred at the previous time level
cur = zeros(Nt+1)                       # current density calculated from fl
ux

# Set initial condition u(x,0) = cox, uu(x,0) = cred
for i in range(0, Nx+1):
    u_1[i] = cox
    uu_1[i] = cred

# Time loop (explicit integration of equations- no iteration required)
for n in range(0, Nt+1):
    # Compute u at inner mesh points
    for i in range(1, Nx):
        # Calculate new concentrations based on values from previous time
step
        u[i] = u_1[i] + FFox*(u_1[i-1] - 2*u_1[i] + u_1[i+1])
        uu[i] = uu_1[i] + FFred*(uu_1[i-1] - 2*uu_1[i] + uu_1[i+1])

    # Insert boundary conditions far away from surface
    u[Nx] = cox
    uu[Nx] = cred
    # Boundary condition at surface- calculate concentrations from applied
 potential and flux B.C.
    E = Estart + vscan*t[n]
    ratio = exp(neq*F/R/T*(E-Unot))
    uu[0] = (uu[1]+Dox/Dred*u[1])/(Dox/Dred*ratio+1)
    u[0]=uu[0]*ratio
```

Out[8]: <matplotlib.text.Text at 0x8d9f9f0>



In [ ]:

Use data from Appendix A or Appendix C to determine values of U^{θ} for the following

a. A lead–acid battery (both lead and lead oxide both react to form lead sulfate)
b. A zinc–air battery in alkaline media

a) The overall reaction for the lead acid cell is

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_3O^+} + 2\mathrm{HSO_4^-} \rightarrow 2\mathrm{PbSO_4} + 4\mathrm{H_2O}$$

$$U = U^{\theta}_{\mathrm{PbO_2}} - U^{\theta}_{\mathrm{Pb}}$$

The terms on the right side correspond to entries 2 and 17 in appendix A

$$U = 1.685 - (-0.356) = \boxed{2.0141\ \mathrm{V}}$$

b) For the zinc air cell

$$\mathrm{Zn} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{ZnO}$$

At the positive electrode

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e^-} \rightarrow 4\mathrm{OH^-}$$

Appendix A gives the standard potential for this reaction as 0.401 V

At the negative electrode, subtracting

$$\begin{array}{r} 2\mathrm{Zn} + \mathrm{O_2} \rightarrow 2\mathrm{ZnO} \\ \mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e^-} \rightarrow 4\mathrm{OH^-} \\ \hline 2\mathrm{Zn} + 4\mathrm{OH^-} \rightarrow 2\mathrm{ZnO} + 4\mathrm{e^-} + 2\mathrm{H_2O} \end{array}$$

this reaction does not appear in the table, however, we can use data from Appendix C for the Gibbs energy of formation of ZnO

$$U^{\theta} = \frac{-\Delta G_f^o}{nF} = \frac{320{,}480}{(2)(96485)} = \boxed{1.661\ \mathrm{V}}$$

Sodium is far more abundant in the earth's crust than lithium. Consequently, there is interest in replacing lithium as the negative electrode material with sodium in batteries. Consider the overall reaction of lithium with cobalt as an example for a new secondary battery.

$$\mathrm{CoO} + 2\mathrm{Li} \leftrightarrow \mathrm{Co} + \mathrm{Li_2O}.$$

a. Write the equivalent reaction where sodium replaces lithium. Categorize this reaction based on the discussion from Section 7.2.
b. Using the thermodynamic data provided in Appendix C, calculate the equilibrium potential, capacity in A·h g^{-1}, and specific energy for lithium and sodium versions of this battery.

a)

$$\mathrm{CoO} + 2\mathrm{Na} \leftrightarrow \mathrm{Co} + \mathrm{Na_2O}.$$

This is a reconstruction/displacement reaction. Some of you may be familiar with lithium-ion batteries and be tempted to describe this as an insertion reaction, but that is not the case here. One type of lithium-ion battery uses lithium cobalt oxide for the positive electrode, where the metal oxide forms a stable host into which lithium is inserted. In this reaction, there is no stable host and it is clearly a conversion reaction. See "Conversion reactions for sodium batteries," F. Klein et al., *Phys. Chem. Chem. Phys*., **15** 15876 (2013).

b) From Appendix C

$$-\Delta G^o_{f,\mathrm{CoO}} = -214.221 \text{ kJ mol}^{-1}$$
$$-\Delta G^o_{f,\mathrm{Li_2O}} = -561.911 \text{ kJ mol}^{-1}$$
$$-\Delta G^o_{f,\mathrm{Na_2O}} = -376.560 \text{ kJ mol}^{-1}$$

$$U^\theta_{\mathrm{Li/Co}} = \frac{-\Delta G^o_{f,Rx}}{nF} = \frac{-(-561{,}911 + 214{,}221)}{(2)(96485)} = \boxed{1.802 \text{ V}}$$

$$U^\theta_{\mathrm{Na/Co}} = \frac{-\Delta G^o_{f,Rx}}{nF} = \frac{-(-376{,}560 + 214.221)}{(2)(96485)} = \boxed{0.841 \text{ V}}$$

The capacities in A·h are determined on the basis of one mole of CoO

For the Li version

$$\frac{1 \text{ mol CoO}}{}\left|\frac{2 \text{ eq.}}{\text{mol CoO}}\right|\frac{96485 \text{ C}}{\text{eq.}}\left|\frac{\text{Ah}}{3600 \text{ C}}\right|\frac{\text{mol}}{88.81 \text{ g}} = 604 \text{ mA} \cdot \text{h g}^{-1}$$

For the Na version

$$\frac{1 \text{ mol CoO}}{}\left|\frac{2 \text{ eq.}}{\text{mol CoO}}\right|\frac{96485 \text{ C}}{\text{eq.}}\left|\frac{\text{Ah}}{3600 \text{ C}}\right|\frac{\text{mol}}{120.93 \text{ g}} = 444 \text{ mA} \cdot \text{h g}^{-1}$$

The theoretical specific energy is the product of the capacity and the equilibrium potential.

Fop Li

$$0.604 \times 1.802 = 1.09 \text{ Wh g}^{-1}$$

Fop Na

$$0.444 \times 0.841 = 0.373 \text{ Wh g}^{-1}$$

A common primary battery for pacemakers is the lithium–iodine cell. The negative electrode is lithium metal, the positive electrode is a paste made with I_2 and a small amount of polyvinylpyridine (PVP), and the separator is the ionic salt LiI. The overall reaction is

$$2\text{Li} + \text{I}_2 \rightarrow 2\text{LiI(s)}$$

Write out the half-cell reactions and, using the data from Appendix A, calculate the equilibrium potential and the theoretical capacity in A·h g^{-1}. You may treat the positive-electrode paste as pure iodine. Categorize this reaction based on the discussion from Section 7.2.

At the negative electrode

$$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$$

At the positive electrode

$$\tfrac{1}{2}\text{I}_2 + \text{e}^- \rightarrow \text{I}^-$$

$$\text{Li}^+ + \text{I}^- \rightarrow \text{LiI(s)}$$

From Appendix C

$$-\Delta G^o_{f,\text{LiI}} = -270.300 \text{ kJ mol}^{-1}$$

$$U^\theta_{\text{LiI}} = \frac{-\Delta G^o_{f,Rx}}{nF} = \frac{-(-270{,}300)}{(1)(96485)} = 2.801 \text{ V}$$

The reaction is a restructuring/formation reaction.

The theoretical capacity is

$$\frac{1 \text{ mol Li}}{}\left|\frac{1 \text{ eq.}}{\text{mol Li}}\right|\frac{96485 \text{ C}}{\text{eq.}}\left|\frac{\text{Ah}}{3600 \text{ C}}\right|\frac{\text{mol}}{(6.941 + 126.904) \text{ g}} = 200 \text{ mA} \cdot \text{h g}^{-1}$$

The lithium–iodine cell described in Problem 7.3 is used for an implantable pacemaker. Note that LiI is produced during discharge, and this salt adds to the thickness of the separator. The nominal current is 28 μA and is assumed constant over the life of the cell. How much active material is needed for a 5 year life? At 37 °C, the LiI electrolyte has an ionic conductivity of 4×10^{-5} S m^{-1}. If the separator is formed in place from the overall reaction, and LiI has a density of 3494 kg m^{-3}, what is the voltage drop across the separator due to ohmic losses in the separator after 2.5 years? The cell area is 13 cm^2. Please comment on the magnitude of the voltage drop. Is it important? Why or why not?

The active material needed is

$$\frac{28 \times 10^{-6}\ \text{C}}{6}\left|\frac{5\ \text{yr}}{}\right|\frac{365\ \text{day}}{\text{yr}}\left|\frac{24\ \text{h}}{\text{day}}\right|\frac{3600\ \text{s}}{\text{h}}\left|\frac{\text{A}\cdot\text{h}}{3600\ \text{C}}\right. = 1.226\ \text{A}\cdot\text{h}$$

From problem 7.3, the capacity is $0.20\ \text{A}\cdot\text{h}\ \text{g}^{-1}$

$$\frac{1.226\ \text{A}\cdot\text{h}}{}\left|\frac{\text{g LiI}}{0.2\text{A}\cdot\text{h}}\right. = 6.12\ \text{g LiI}$$

Next the ohmic loss is calculated.

$$\Delta V = \frac{L}{\kappa}\frac{I}{A} = \frac{tIM}{F\kappa\rho A}\frac{I}{A} = 0.29\ \text{V}$$

The potential drop due to resistance is about 10 % of the equilibrium potential. For continuous operation at this low current, the ohmic polarization is not a major issue, but the high resistance does limit the power that can be achieved.

Most high-energy cells use lithium metal for the negative electrode; furthermore, rechargeable lithium systems rely on intercalation for reversible reactions at the cathode. Discuss the idea of replacing Li with Mg for future rechargeable cells. Specifically contrast and compare Li and Mg commenting on

a. Specific capacity [A·h g-metal^{-1}]

b. Volumetric capacity [A·h cm^{3}-metal^{-1}]

c. Earth abundance

d. Specific energy and energy density

e. Ionic radii

f. Charge/radius ratio (Hint: how is this likely to affect intercalation?)

a) Specific capacity

$$\frac{1\ \text{mol Li}}{}\left|\frac{1\ \text{eq.}}{\text{mol}}\right|\frac{96485\ \text{C}}{\text{eq.}}\left|\frac{\text{mol}}{6.941\ \text{g}}\right|\frac{\text{A}\cdot\text{h}}{3600\ \text{C}} = 3.86\ \text{A}\cdot\text{h g}^{-1}$$

$$\frac{1\ \text{mol Mg}}{}\left|\frac{2\ \text{eq.}}{\text{mol}}\right|\frac{96485\ \text{C}}{\text{eq.}}\left|\frac{\text{mol}}{24.305\ \text{g}}\right|\frac{\text{A}\cdot\text{h}}{3600\ \text{C}} = 2.21\ \text{A}\cdot\text{h g}^{-1}$$

b) volumetric capacity,

$$\frac{3.86\ \text{A}\cdot\text{h}}{\text{g}}\left|\frac{0.534\ \text{g}}{\text{cm}^3}\right. = 2.06\ \text{A}\cdot\text{h cm}^{-3}$$

$$\frac{2.21\ \text{A}\cdot\text{h}}{\text{g}}\left|\frac{1.738\ \text{g}}{\text{cm}^3}\right. = 3.84\ \text{A}\cdot\text{h cm}^{-3}$$

c) Earth abundance, retrieved from
https://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth%27s_crust

Li ~0.002 %
Mg ~3 %

d) Theoretical specific energy and energy density. Use standard potentials from Appendix A.

$Li^+ + e^- \rightarrow Li$	-3.045
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.357

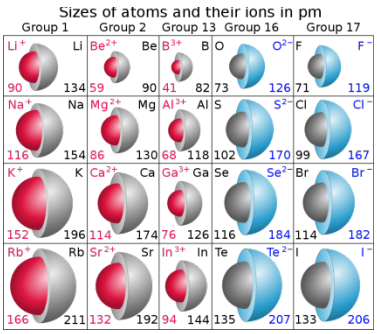
$$\frac{3.86\ \mathrm{A\cdot h}}{\mathrm{g}}\left|\frac{3.045\ \mathrm{V}}{}\right. = 11.8\ \mathrm{W\cdot h\ g^{-3}}$$

$$\frac{2.21\ \mathrm{A\cdot h}}{\mathrm{g}}\left|\frac{2.357\ \mathrm{V}}{}\right. = 5.2\ \mathrm{W\cdot h\ g^{-3}}$$

$$\frac{11.8\ \mathrm{W\cdot h}}{\mathrm{g}}\left|\frac{0.534\ \mathrm{g}}{\mathrm{cm^3}}\right. = 6.3\ \mathrm{W\cdot h\ cm^{-3}}$$

$$\frac{5.2\ \mathrm{W\cdot h}}{\mathrm{g}}\left|\frac{1.738\ \mathrm{g}}{\mathrm{cm^3}}\right. = 9.1\ \mathrm{W\cdot h\ cm^{-3}}$$

e) Ionic radii
https://en.wikipedia.org/wiki/Ionic_radius
We see that the relative size of the two ions are about the same.



https://environmentalchemistry.com/yogi/periodic/ionicradius.html

Li 76 pm
Mg 72 pm

There is not a large difference between the two, so Mg will not face a different steric barrier.

The charge ratio, charge/radius is about two time larger for Mg2+. Thus, Mg will have strong electrostatic interactions making intercalation more difficult.

The carbon monofluoride primary cell consists of a lithium metal negative electrode, and a carbon monofluoride CF_x as the positive electrode. The carbon monofluoride is produced by the direct fluorination of coke or another carbon. The fluorine expands the carbon structure creating a nonstoichiometric intercalation material; the value of *x* is about 1. The overall reaction is expressed as

$$x\mathrm{Li} + \mathrm{CF}_x \leftrightarrow x\mathrm{LiF} + \mathrm{C}.$$

a. If the equilibrium potential of this cell is about 3.0 V and *x*=0.95, determine the theoretical specific energy of this battery. How does this value compare to the capacity of a commercial cell, which is about 450 W·h kg^{-1}? Why are they different?
b. Calculate the theoretical specific energy of the lithium sulfur dioxide battery (Table 7-1) and compare it to that of the CFx cell.

a) Specific energy

$$\frac{1\ \mathrm{mol\ Li}}{}\left|\frac{1\ \mathrm{eq.}}{\mathrm{mol}}\right|\frac{96485\ \mathrm{C}}{\mathrm{eq.}}\left|\frac{\mathrm{mol}}{37.95\ \mathrm{g}}\right|\frac{\mathrm{A\cdot h}}{3600\ \mathrm{C}}\left|\frac{3.0\ \mathrm{V}}{}\right. = 2119\ \mathrm{W\cdot h\ kg^{-1}}$$

The practical battery has less than a quarter of this theoretical value.

for the lithium sulfur dioxide battery

$$2\mathrm{Li} + 2\mathrm{SO}_2 \rightarrow \mathrm{Li}_2\mathrm{S}_2\mathrm{O}_4$$

$$\frac{1\ \mathrm{mol\ Li}}{}\left|\frac{1\ \mathrm{eq.}}{\mathrm{mol}}\right|\frac{96485\ \mathrm{C}}{\mathrm{eq.}}\left|\frac{\mathrm{mol}}{71.01\ \mathrm{g}}\right|\frac{\mathrm{A\cdot h}}{3600\ \mathrm{C}}\left|\frac{3.0\ \mathrm{V}}{}\right. = 1132\ \mathrm{W\cdot h\ kg^{-1}}$$

Roughly half that of the carbon monofluoride cell

Calculate the standard potential, U^{θ}, for the Ni/Fe (Edison cell) from the information below for the half-cell reactions.

$$\mathrm{Fe} + 2\mathrm{OH}^- \leftrightarrow \mathrm{Fe(OH)_2} + 2\mathrm{e}^- \qquad \text{(-0.89 V vs. SHE)}$$
$$\mathrm{NiOOH} + \mathrm{e}^- + \mathrm{H_2O} \leftrightarrow \mathrm{Ni(OH)_2} + \mathrm{OH}^- \qquad \text{(0.290V vs. Ag/AgCl)}$$

The overall reaction is

$$\mathrm{Fe} + 2\mathrm{NiOOH} + 2\mathrm{H_2O} \leftrightarrow \mathrm{Fe(OH)_2} + \mathrm{Ni(OH)_2}$$

At the positive electrode,

$$\mathrm{NiOOH} + \mathrm{e}^- + \mathrm{H_2O} \leftrightarrow \mathrm{Ni(OH)_2} + \mathrm{OH}^- \qquad \text{(0.290V vs. Ag/AgCl)}$$

Add potential of silver chloride potential to this value

$$0.29 + 0.222 = 0.512 \text{ V}$$

Subtract the negative from the positive to obtain the cell potential

$$U = U_+ - U_- = 0.512 - (-0.89) = 1.402 \text{ V}$$

Calculate the theoretical specific energy of the aluminum–air battery. The two electrode reactions are

$$\mathrm{Al} + 3\mathrm{OH}^- \leftrightarrow \mathrm{Al(OH)_3} + 3\mathrm{e}^- \qquad \text{(-2.31 V)}$$

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4\mathrm{e}^- \leftrightarrow 4\mathrm{OH}^- \qquad \text{(0.401 V)}$$

Balance the two equations, add together

$$4\mathrm{Al} + 12\mathrm{OH}^- \leftrightarrow 4\mathrm{Al(OH)_3} + 12\mathrm{e}^-$$

$$3\mathrm{O_2} + 6\mathrm{H_2O} + 12\mathrm{e}^- \leftrightarrow 12\mathrm{OH}^-$$

$$4\mathrm{Al} + 3\mathrm{O_2} + 6\mathrm{H_2O} \leftrightarrow 4\mathrm{Al(OH)_3}$$

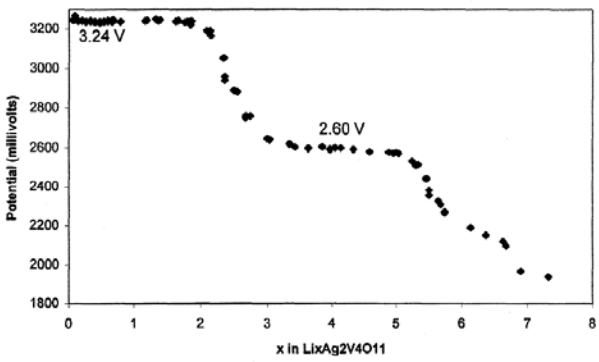
with a potential of $0.401 - (-2.31) = 2.711\ \mathrm{V}$

Basis of 1 g of active material (here we include, Al, O_2, and H_2O)

$$\frac{1\ \mathrm{g}}{}\left|\frac{1\ \mathrm{mol}}{4(27)+6(16)+6(18)\mathrm{g}}\right|\frac{12\mathrm{eq.}}{\mathrm{mol}}\left|\frac{96485\ \mathrm{C}}{\mathrm{eq.}}\right|\frac{2.711\ \mathrm{V}}{}\left|\frac{\mathrm{A}\cdot\mathrm{h}}{3600\ \mathrm{C}}\right. = 2.8\ \mathrm{W}\cdot\mathrm{h\ g^{-1}}$$

Some implantable batteries must provide high-pulse power for short periods of time, a defibrillator for instance. This requirement that cannot be met with the Li/I_2 cell (problems 3 and 4). One battery for such a device is the lithium silver–vanadium–oxide cell (Li/SVO) cell. The overall reaction is

$$x\text{Li} + \text{Ag}_2\text{V}_4\text{O}_{11} \rightarrow \text{Li}_x\text{Ag}_2\text{V}_4\text{O}_{11}$$



$Ag_2V_4O_{11}$ is a highly ordered crystalline material consisting of vanadium oxide sheets alternating with silver ions. These layers persist with the lithiation of the material. The equilibrium potential is shown on the right. There are two plateaus followed by a sloping decrease in potential at $x > 5$. What does this behavior suggest about the phases of the products? Assuming that the potential must be greater than or equal to that of the 2nd plateau, calculate the theoretical energy density and specific energy of this battery.

The positive electrode is a binary metal oxide of silver and vanadium, either may be reduced during discharge. The two plateaus suggest that these two phases are present during intercalation. The first plateau is associated with the reduction of vanadium, and the second is associated with the reduction of silver.

Basis of 1 mol of $Li_5Ag_2V_4O_{11}$,

$$2(107.86) + 4(50.94) + 11(16) + 4(6.941) = 630.2\text{g mol}^{-1}$$

Find the capacity in terms of x

$$\frac{1\text{ mol}}{630.2\text{g}}\left|\frac{x\text{ eq.}}{\text{mol}}\right|\frac{96485\text{ C}}{\text{eq.}}\left|\frac{\text{A}\cdot\text{h}}{3600\text{ C}}\right. = 42.5x\text{ mA}\cdot\text{h g}^{-1}$$

Energy is obtained by summing over the plateaus

$$= 42.5\sum_i \Delta x_i\, V_i$$

$$\text{capacity} = \left\{\begin{matrix} 3.24(2) \\ +\ 2.8(1) \\ +\ 2.6(2) \end{matrix}\right\} 42.5 = 615\text{ mW}\cdot\text{h g}^{-1}$$

Assuming a density of 6 g cm^{-3},

$$\frac{0.615\text{W}\cdot\text{h}}{\text{g}}\left|\frac{6000\text{g}}{\text{L}}\right. = 615\text{ W}\cdot\text{h L}^{-1}$$

Li ions are shuttled between electrodes of a lithium-ion battery during operation. During the charging process, lithium ions are transported from the positive electrode to the negative electrode. For a binary electrolyte (lithium salt, LiX, in an organic solvent), sketch the concentration of the salt in the separator of the cell. Explain the profile and comment on how it would change with changes in the magnitude and/or direction of the current density, *i*.

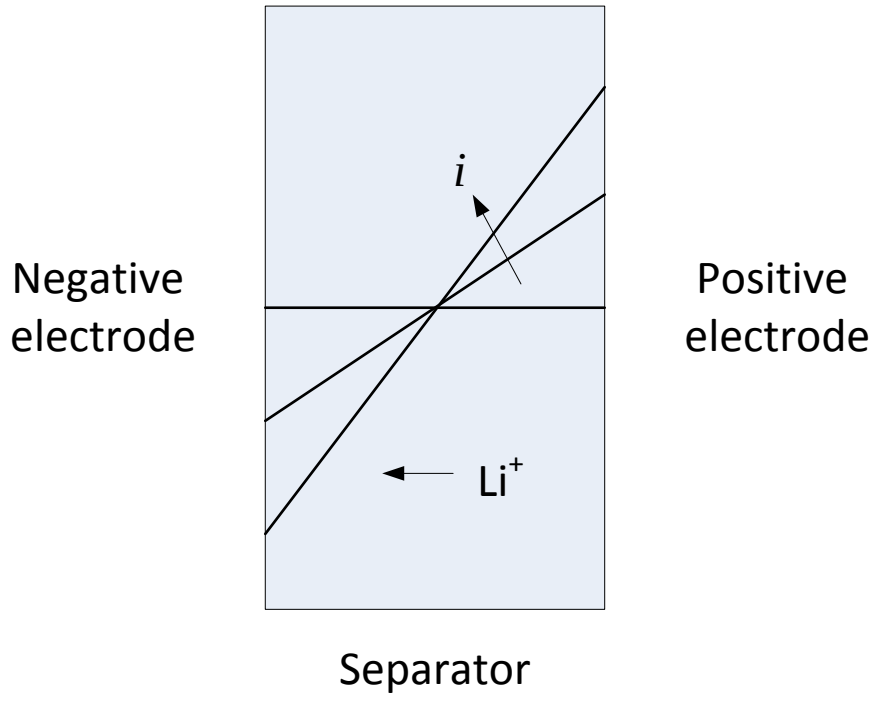
The ions move due to both concentration gradients and migration. The anion, X^-, is not involved in the reaction, but because of electroneutrality $c = c_{Li^+} = c_{X^-}$. Assuming a quasi-steady state, the flux of anions is zero so that the gradient in potential that drives migration of the anion must be balanced with a concentration gradient.

From Equation 7.15,

$$\frac{i}{F} = \frac{-D}{(1 - t_+^o)} \frac{dc}{dx}$$

If the diffusivity and transference number are constants, the concentration varies linearly. Li^+ moves from high to low potential in the separator, X^- is driven the other way by the electric field. Therefore, the slope for concentration must be positive.

As is evident from the equation, as the current density increases, the slope increases. If the direction of current is reversed (discharging) then the slope would change sign.



For an ohmically limited battery, the potential of the cell is given by $V_{cell}=U–IR_{int}$, where R_{int} is the internal resistance of the cell. Derive an expression for the maximum power. At what current and cell potential does is the maximum power achieved? How are the results changed if there is a cutoff potential, V_{co}, below which operation of the cell is not recommended, that is reached first (i.e., before the maximum power)?

The power is

$$P = IV = I(U - IR_{\text{int}})$$

The maximum is determined by setting the derivative to zero

$$\frac{dP}{dI} = 0 = U - 2IR_{\text{int}}$$

so

$$I = \frac{U}{2R_{\text{int}}}$$

Thus,

$$V_{cell} = U - IR_{\text{int}} = \frac{U}{2}$$

and

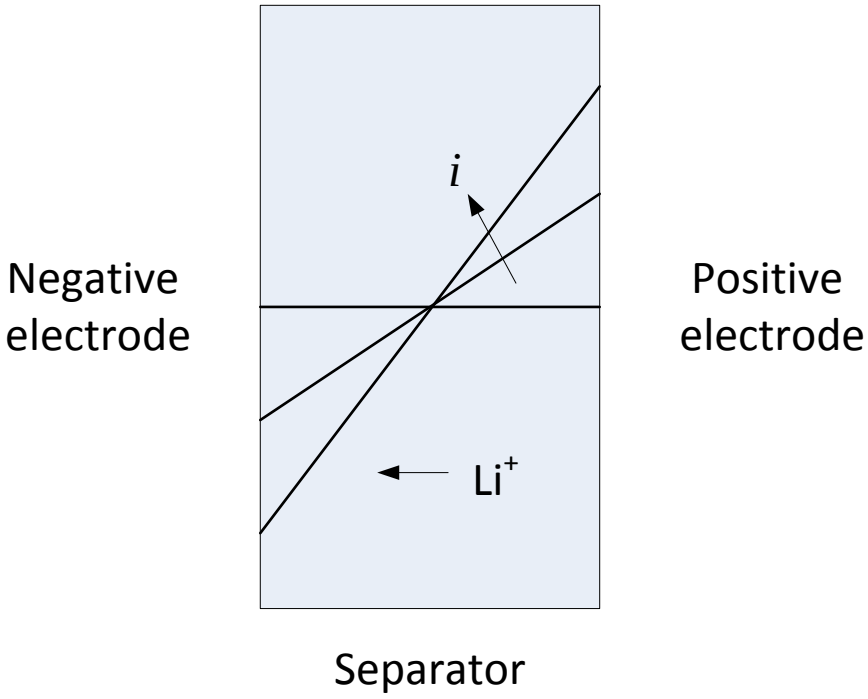
$$P_{max} = IV = \frac{U^2}{4R_{\text{int}}}$$

If there is a cutoff potential that is greater than $U/2$, then the power is limited to $V_{cell} = V_{co}$

$$I = \frac{U - V_{co}}{R_{\text{int}}}$$

and

$$P_{max} = \frac{V_{co}(U - V_{co})}{R_{\text{int}}}$$


Negative
electrode
i
Positive
electrode
Li+
Separator

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"Problem 7-12"

Pmax=1 [W]; "maximum power"
A=0.0015 [m^2]
U=2.60 [V]; "examine two steps in curve for U, try both 3.24 and 2.60 V"

Pmax=U*U*A/(4*Rint)

current=U/2/Rint

cf=1e4 [cm^2/m^2]
Rdc=Rint*cf; "maximum value in resistance to acheive desired power"

"for the first voltage plateau, 3.24 V, the maximum resistance would be about 40 ohm-m^2, there is no issue here"

"on the second voltage plateau, 2.6 V, the maximum resistance would be 25 ohm-m^2, which corresponds to a value for x of about 4. "

SOLUTION
Unit Settings: SI C kPa J mass deg

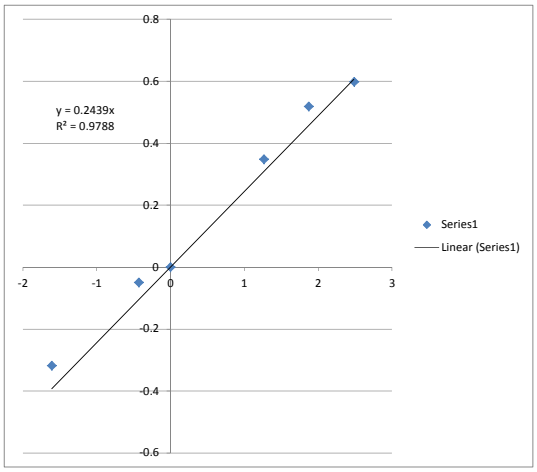
A = 0.0015 [m^2]
current = 512.8 [A/m^2]
Rdc = 25.35 [Ω-cm^2]
U = 2.6 [V]

cf = 10000 [cm^2/m^2]
Pmax = 1 [W]
Rint = 0.002535 [Ω-m^2]

No unit problems were detected.

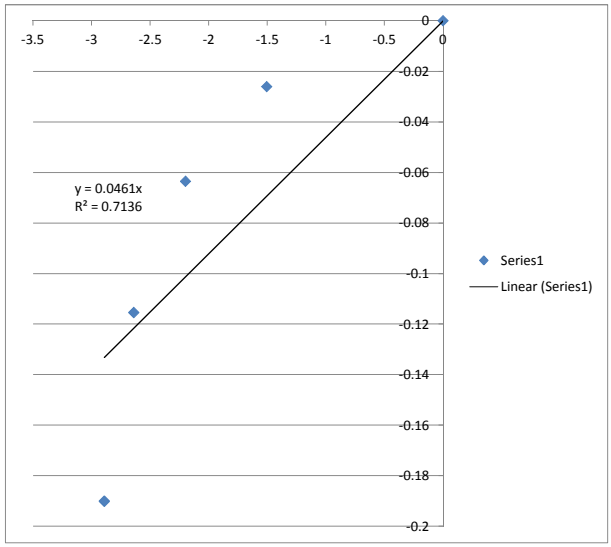
Current	C-rate	ratio	time, hours	C, Ah	Peukert	Cp, capacity	ln(Cp)	ln (Crate)
3.9	5.45	5.00	0.13	0.52	0.69	0.73	-0.31845	-1.60944
1.2	1.68	1.54	0.57	0.68	0.91	0.95	-0.05019	-0.43078
0.78	1.09	1.00	0.92	0.72	1.00	1.00	0	0
0.22	0.31	0.28	4.60	1.01	1.34	1.42	0.347401	1.265666
0.12	0.17	0.15	10.00	1.20	1.54	1.68	0.517794	1.871802
0.065	0.09	0.08	20.00	1.30	1.77	1.82	0.597837	2.484907

The fit is reasonable. k=1.24



C-rate	C, Ah	Peukert	Cp, capacit	ln(Cp)	ln (Crate)
1	7.8	1.00	1	0	0
4.5	7.6	7.28	0.974359	-0.02598	-1.50408
9	7.32	7.05	0.938462	-0.06351	-2.19722
14	6.95	6.90	0.891026	-0.11538	-2.63906
18	6.45	6.82	0.826923	-0.19004	-2.89037

The fit is not very good. k=1.0461
The Peukert equation over predicts capacity at high C-rates
We might expect that an increase in temperature would reduce polarizations and make the Peukert equation underpredict the capacity. For these data, the Peukert equation is not accurate.



What is the theoretical specific capacity and energy for the Leclanché cell? The overall reaction is

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$$

Use 1.6 V as the average potential of the cell. A practical battery of this chemistry has a specific energy of about 85 $W \cdot h\ kg^{-1}$. Please explain the difference between the theoretical and practical values.

The positive electrode is a binary metal oxide of silver and vanadium, either may be reduced during discharge. The two plateaus suggest that these two phases are present during intercalation. The first plateau is associated with the reduction of vanadium, and the second is associated with the reduction of silver.

at the negative electrode

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$\frac{\text{mol Zn}}{0.06539\ \text{kg}}\left|\frac{2\ \text{eq.}}{\text{mol}}\right|\frac{96485\ \text{C}}{\text{eq.}}\left|\frac{\text{A} \cdot \text{h}}{3600\ \text{C}}\right. = 819.74\ \text{A} \cdot \text{h kg}^{-1}$$

For 1 kg of Zn, find mass of manganese oxides

$$\frac{\text{mol Zn}}{0.06539\ \text{kg}}\left|\frac{2\ \text{mol}\ MnO_2}{\text{mol Zn}}\right|\frac{0.08693\ \text{kg}}{\text{mol}\ MnO_2} = 2.66\ \text{kg}$$

Specific capacity is

$$= \frac{819.74\ \text{A} \cdot \text{h}}{1\text{kg} + 2.66\text{kg}} = 224\ \text{A} \cdot \text{h kg}^{-1}$$

specific energy

$$= 224\ \times 1.6\ \text{V} = 358\ \text{W} \cdot \text{h kg}^{-1}$$

Calculate the theoretical specific energy for the lithium–air cell. Base your answer on the mass of lithium only. There are three possible reactions

$$4\text{Li} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH}_{(\text{aq})}$$
$$4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O}$$
$$2\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O}_2$$

From Appendix C, find the following data for Gibbs energy of formation

H_2O	-237.129 kJ mol^{-1}
Li_2O	-561.2 kJ mol^{-1}
Li_2O_2	-571.1 kJ mol^{-1}
LiOH	-451.1 kJ mol^{-1}

For 1 g of Li, the capacity is

$$\frac{1\text{ g Li}}{}\left|\frac{\text{mol Li}}{6.941\text{ g}}\right|\frac{1\text{ eq.}}{\text{mol}}\left|\frac{96485\text{ C}}{\text{eq.}}\right|\frac{\text{A}\cdot\text{h}}{3600\text{ C}} = 3861\text{ mA}\cdot\text{h g}^{-1}$$

Multiply by the theoretical potential to get energy

a) first possible reaction

$$U = \frac{-\Delta G^o_{Rx}}{nF} = \frac{4(451{,}100) - 2(237{,}129)}{(4)96485} = 3.45\text{ V}$$

For 1 kg of Zn, find mass of manganese oxides

$$\frac{\text{mol Zn}}{0.06539\text{ kg}}\left|\frac{2\text{ mol MnO}_2}{\text{mol Zn}}\right|\frac{0.08693\text{ kg}}{\text{mol MnO}_2} = 2.66\text{ kg}$$

Specific energy is

$$= 3861\ \times 3.45\text{ V} = 13.307\text{ W}\cdot\text{h g}^{-1}$$

similarly for the other reactions

b) U=2.91 V 11.237 W·h g^{-1}

b) U=3.10 V 11.970 W·h g^{-1}

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problem 7-17

$L_s = 0.000025$ [m]

$k_{eff} = 0.002$ [1/(Ω-m)]

$k = 0.018$ [1/(Ω-m)]

$\varepsilon = 0.55$

$$k_{eff} = k \cdot \frac{\varepsilon}{\tau}$$

$$\Delta V = i \cdot \frac{L_s}{k_{eff}}$$

$i = 4$ [A/m^2]

SOLUTION

Unit Settings: SI C kPa J mass deg

$\Delta V = 0.05$ [V]
$i = 4$ [A/m^2]
$k_{eff} = 0.002$ [1/(Ω-m)]
$\tau = 4.95$
$\varepsilon = 0.55$
$k = 0.018$ [1/(Ω-m)]
$L_s = 0.000025$ [m]

No unit problems were detected.

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problem 7-18

Cell Efficiency

n is the number of cycles
cr is the ratio of capacity to initial capacity,
and eta is the coulombic efficiency

n = 100

cr = 0.8

$$\ln[\eta] = \frac{\ln[cr]}{n}$$

SOLUTION
Unit Settings: SI C kPa kJ mass deg
cr = 0.8
n = 100

η = 0.9978

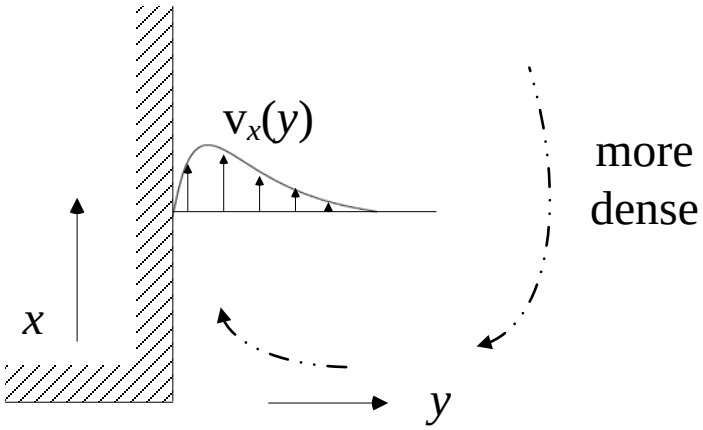
No unit problems were detected.

During discharge of a lead–acid battery, the following reaction takes place at the positive electrode

$$PbO_2 + 2H^+ + 2e^- + H_2SO_4 \rightarrow PbSO_4 + 2H_2O$$

Discharge of a vertical PbO_2 electrode results in flow due to natural convection. Briefly explain the natural convection process on the electrode. Sketch the velocity profile near the positive electrode.

During discharge sulfuric acid is consumed and water produced. Since sulfuric acid is more dense than water, the density of the electrolyte near the electrode decreases. Buoyancy forces will cause the fluid to rise near the electrode, and more dense fluid (higher concentration of acid) will replace the rising less dense fluid. This is an analogous situation as that shown in Figure 4.8. Here, the density difference is due to compositional changes rather than temperature



Velocity is zero at the surface (no slip condition) and also zero far from the electrode (outside the boundary layer)

A lithium-ion battery is being discharged with a current density of i mA cm^{-2}. The positive electrode has a porous structure, and the electronic conductivity is much greater than the ionic conductivity, $\sigma >> \kappa$. Assume an open-circuit plateau, where U^+ is essentially flat, but increases for high SOC and drops for low SOC.

a) Sketch the ionic current density, i_2, across the separator and porous electrode at the start of the discharge.

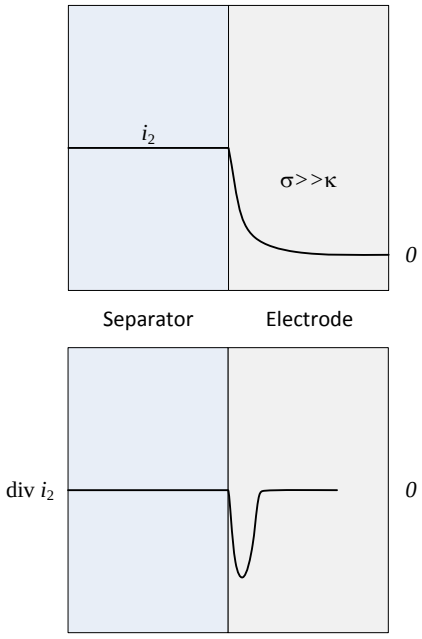
b) Sketch the divergence of the current density; physically explain the shape of this curve.

c) Repeat (a) and (b) when the cell has nearly reached the end of its capacity. Again explain the shape?

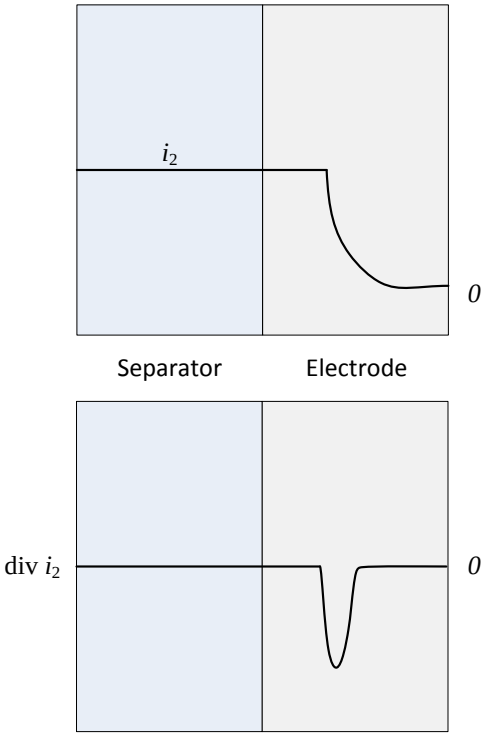
d) How would the internal resistance change with depth of discharge for this cell?

a, b)

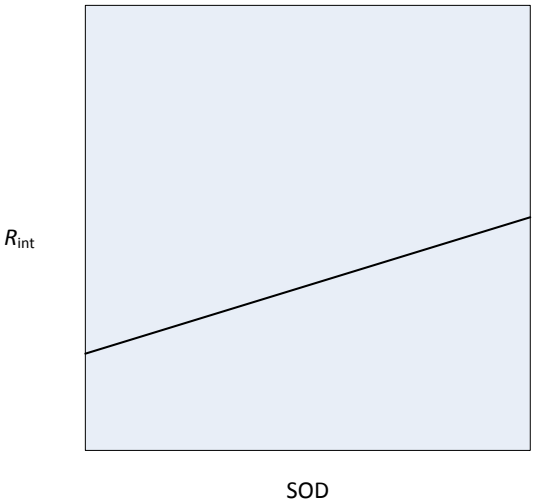
Because the electronic conductivity is much higher than the ionic, the reaction is skewed to the front of the electrode. There is a sharp spike in the divergence corresponding to the location of the reaction.



c) As the reaction proceeds, the active material in the front of the electrode will be used up, shifting the local equilibrium potential. The reaction moves toward the back of the electrode, with a spike traveling across the electrode during discharge

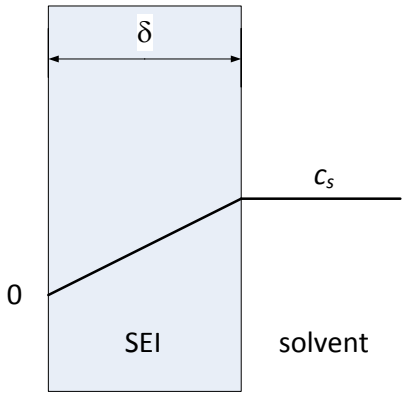


d) As the reaction proceeds the ionic path will increase, thus the internal resistance will increase with increasing state of discharge (SOD).



Develop a simple model for growth of SEI formation in lithium-ion cells. Assume the rate-limiting step is the diffusion of solvent through the film. Show that the thickness of the film is proportional to the square root of time. Discuss how capacity and power fade would evolve under these conditions.

Model assumes that the reaction is limited by diffusion of solvent through SEI. We also make a pseudo-steady state assumption, namely that diffusion is rapid compared to reaction rate



$$\text{rate} = \frac{Dc_s}{\delta}$$

The rate of growth is

$$\frac{d\delta}{dt} = \left(\frac{Dc_s}{\delta}\right)\frac{s_i M_i}{\rho}$$

s_i stoichiometric coefficient

M_i molecular weight'

ρ density of film

rearrange the differential equation

$$\delta d\delta = \frac{Dc_s s_i M_i}{\rho} dt$$

integrate

$$\delta^2 = \frac{2Dc_s s_i M_i}{\rho} t$$

or

$$\delta = \sqrt{\frac{2Dc_s s_i M_i}{\rho} t}$$

Lithium is lost (not available for cycling) in proportion to the thickness of the SEI. Thus, lithium is lost proportional to the square root of time and thus the capacity of the cell will decrease linearly with the square root of time. Thus, capacity fade will be large at first, but then the rate of change will be reduced.

Starting with Equation 7-20, which gives the rate of heat generation in the absence of any side reactions or short circuits, develop an expression for the rate of heat generation as a function of current. Treat the cell as being ohmically limited with a resistance R_Ω. You may also consider that the entropic contribution, $\partial U/\partial T$, is constant. Finally, assume that there is an additional, constant rate of heat generation due to self-discharge, $\dot{q}_{sd}$. Sketch the rate of heat generation as a function of current for the cell.

$$\dot{q} = I(U - V_{cell}) - I\left(T\frac{\partial U}{\partial T}\right) \quad \text{[W]} \tag{7-20}$$

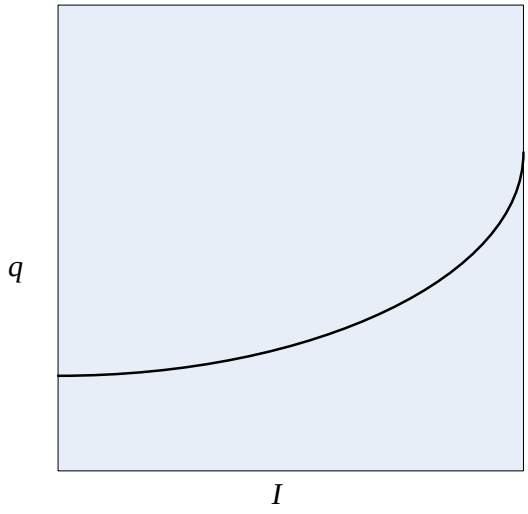
For an ohmically limited cell

$$V_{cell} = U - iR_\Omega$$

substituting

$$\dot{q} = I^2 R_\Omega - IT\left(\frac{\partial U}{\partial T}\right)$$

$$\dot{q}_t = \dot{q} + \dot{q}_{sd} = I^2 R_\Omega - IT\left(\frac{\partial U}{\partial T}\right) + \dot{q}_{sd}$$



The rate of self-discharge is critical design parameter for primary batteries.

a. Assume that a primary battery is designed to last for 5 years at a constant average discharge rate. At what C-rate does this battery operate?
b. For this same cell, what is the equivalent C-rate for the self-discharge process if the current efficiency is to be kept above 90%? Assume that the self-discharge reaction operates as a chemical short in parallel with the main electrochemical reaction.
c. Because of the extremely long lives of some batteries, micro-calorimetry is used to measure the rate of self-discharge. Data for a Li/I_2 cell (described in Problem 7.3) are shown on the right. Estimate the current efficiency of the discharge. The equilibrium potential is 2.80 V, the cell resistance is 650 Ω, and the entropic contribution is 0.0092 J C^{-1} at the cell temperature. Assume a nominal operating current of 70 μA.

I, μA	$\dot{q}$, μW
0.047	5.95
14.5	5.79
31.3	6.63
56.5	7.97
125	15.02

a) The C-rate is the inverse of the discharge time in hours

$$Crate = \frac{1}{(365)(24)(5)} = 0.00002283$$

b)

$$\eta = \frac{Crate}{Crate + SD} = 0.9$$

solve for SD, the equivalent C-rate for self discharge, SD=0.000002537

c) The data show the heat generation rate as a function of current. Plotting these shows a roughly parabolic shape with a non-zero intercept. Equation 7-20

$$\dot{q} = I(U - V_{cell}) - I\left(T\frac{\partial U}{\partial T}\right) \quad [\text{W}] \tag{7-20}$$

assumes that there is no short. With a short, an additional term for heat generation must be added, (sd for self discharge).

$$\dot{q} = I^2 R_\Omega - IT\left(\frac{\partial U}{\partial T}\right) + \dot{q}_{sd}$$

We see from the data that when I=0, $\dot{q} = 6\ \mu\text{W} = \dot{q}_{sd}$.

For an internal short, all of the energy goes to heat. To calculate the equivalent current of the short,

$$\dot{q}_{sd} = I_{sd} U$$

$$I_{sd} = \frac{\dot{q}_{sd}}{U} = \frac{6\ \mu\text{W}}{2.8\ \text{V}} = 2.14\ \mu\text{A}$$

$$\eta = \frac{\dot{q}_{sd}}{U} = \frac{70\ \mu\text{A}}{70+2.14\ \mu\text{A}} = 0.97$$

During charging, oxygen can be evolved at the positive electrode of a lead–acid cell. In order to avoid adding water, this oxygen must be reduced back to water. In the so-called *starved* cell design, the electrolyte is limited so that there is some open porosity in the glass-mat separator. Therefore, oxygen can diffuse to the negative electrode. One set of proposed reactions at the negative electrode is

$$\mathrm{Pb}+0.5\mathrm{O_2} \rightarrow \mathrm{PbO}$$

$$\mathrm{PbO} + \mathrm{H^+} + \mathrm{HSO_4^-} \rightarrow \mathrm{PbSO_4} + \mathrm{H_2O}$$

$$\mathrm{PbSO_4} + \mathrm{H^+} + 2\mathrm{e^-} + \mathrm{H_2SO_4} \rightarrow \mathrm{Pb} + \mathrm{HSO_4^-}$$

What is the net reaction? Describe how the evolution of oxygen at the positive electrode and its reaction at the negative electrode is in effect a shuttle mechanism with oxygen for the lead–acid cell. How does the oxygen reaction impact battery performance during charging? How does it impact performance during overcharge? In other words, what is the impact of overcharging these starved lead–acid cells? Finally, these cells are designed to be sealed from the atmosphere. What is impact of having the cell open to the atmosphere on the rate of self-discharge of the starved cell?

The three reactions can be summed

$$0.5\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H_2O}$$

This is just the opposite of the oxidation of water that occurs at the positive electrode. Thus, we have evolution of oxygen at the positive electrode and reduction at the negative, but no net change in the state of charge of the cell. In effect, oxygen is shuttled between the two electrodes.

If this type of cell were exposed to the atmosphere, the lead in the negative electrode would react to form lead sulfate, $\mathrm{PbSO_4}$, effectively rapidly discharging the battery.

It has been proposed that a small contamination of iron in the electrolyte can result in a shuttle mechanism of self-discharge of nickel–cadmium cells. What is the standard potential for this reaction?

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

The two electrode reactions for the NiCd cell can be represented by

$$NiOOH + e^- + H_2O \rightarrow Ni(OH)_2 + OH^- \qquad U^{\theta}=0.49 \text{ V}$$

$$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^- \qquad U^{\theta}=-0.81 \text{ V}$$

Comment on the plausibility of such a self-discharge mechanism.

The reduction of iron (III) is not listed in Appendix A, but the potential can be found from Gibbs energy of formation data from Appendix C.

$$\Delta G^o_{f,Fe^{2+}} = -84.91 \text{ kJ mol}^{-1}$$

$$\Delta G^o_{f,Fe^{3+}} = -10.71 \text{ kJ mol}^{-1}$$

Thus,

$$U = \frac{-\Delta G^o_{f,Rx}}{nF} = \frac{84{,}910 - 10{,}710}{96485} = 0.77 \text{ V}$$

Since the potentials of both electrodes are below 0.77 V, we would expect to find iron in the reduced state, Fe^{2+}

If the redox potential were in between the potentials of the two electrodes, then a shuttle mechanism could exist that would discharge both electrodes.

The discharge reaction for the lead–acid battery proceeds through a dissolution/precipitation reaction. The two reactions for the negative electrode are

$$\mathrm{Pb} \rightarrow \mathrm{Pb}^{2+} + 2\mathrm{e}^{-},$$

$$\mathrm{Pb}^{2+} + \mathrm{SO}_4^{2-} \rightarrow \mathrm{PbSO}_4.$$

This mechanism is depicted in the figure. A key feature is that lead dissolves from one portion of the electrode but precipitates at another. The solubility of Pb^{2+} is relatively low, around 2 g m^{-3}. How then can high currents be achieved in the lead-acid battery?

a. Assume that the dissolution and precipitation locations are planar electrodes separated by a distance, *d*, of 1mm. Using a diffusivity of 10^{-9} m^2 s^{-1} for the lead ions, estimate the maximum current that can be achieved.
b. Rather than two planar electrodes, imagine a porous electrode that is also 1 mm thick, made from particles with a radius 10 μm packed together with a void volume of 0.5. What is the maximum superficial current here based on the pore diameter?
c. What do these results suggest about the distribution of precipitates in the electrodes?

a) For a planar geometry

$$i_{lim} = \frac{\Delta c D n F}{L}$$

$$\Delta c = \frac{2\,\mathrm{g}}{\mathrm{m}^3}\left|\frac{\mathrm{mol}}{207.2\,\mathrm{g}} = 9.65 \times 10^{-3}\ \mathrm{mol\ m^{-3}}\right.$$

$$i_{lim} = \frac{(9.65 \times 10^{-3})10^{-9}2F}{10^{-3}} = 1.86\ \mathrm{mA\ cm^{-2}}$$

b) estimate pore size based on a particle radius

$$r_p = \frac{\varepsilon}{(1-\varepsilon)}\frac{r}{3} = 3.3\ \mu\mathrm{m}$$

Assume distance is $2r_p$, then find current density normal to surface

$$i_{n,lim} = \frac{\Delta c D n F}{2r_p} = 0.28\ \mathrm{A\ m^{-2}}$$

Then include the entire area for a 1 mm thick porous electrode.

$$i_{\,lim} = aLi_{n,lim} = \left[\frac{3(1-\varepsilon)}{r}\right]Li_{n,lim} = 42\ \mathrm{A\ m^{-2}}$$

c) Still a pretty small current density. Pb and PbSO4 particles may be closer together than the pore diameter.

An 8 A·h Ni–MH cell is charged and discharged adiabatically. The data for the temperature rise are shown in the figure (adapted from *J. Therm. Anal. Calorim.*, **112**, 997 (2013)). Explain the effect of rate on the temperature rise. Comparing the differences between the charging and discharging temperature rise, what can be inferred about the entropic contribution to heat generation? Notice that only during charging a bit above 30 °C, the temperature rise increases sharply. Your colleague suggests that the side reactions of oxygen increase rapidly at high temperatures. Can the evolution and recombination of oxygen explain the results?

Ideally, the heat generation consists of two parts. I^2R (ohmic) and the entropic part, which is proportional to the current. As the rate increases, the ohmic losses increase and the temperature increases at a faster rate. For both charge and discharge, the rate of temperature increase is faster at 2C comparted to C/2.

Near the end of charge, there is a rapid increase in temperature. This is likely the result of electrolysis of water and recombination of hydrogen and oxygen. In this case, all of the energy goes to heat.

Based on the observation that the difference in slopes (C/2 to C) is greater for charging (negative current) than for discharging, we can infer that $\frac{\partial U}{\partial T}$ is positive. However, the NiMH cell is notorious for its poor coulombic efficiency. Oxygen and hydrogen evolution may be occurring during charge even at low states of charge, which results in greater heat generation.

The lithium–sulfur battery uses lithium metal for the negative electrode and sulfur with carbon for the positive electrode. The overall reaction is

$$16\mathrm{Li} + \mathrm{S_8} \rightarrow 8\mathrm{Li_2S}\,.$$

The electrochemical process at the positive electrode goes through a series of sequential formation of lithium sulfides ($\mathrm{Li_2S}_x$), specifically:

$$\mathrm{Li_2S_8} \rightarrow \mathrm{Li_2S_6} \rightarrow \mathrm{Li_2S_4} \rightarrow \mathrm{Li_2S_2} \rightarrow \mathrm{Li_2S}$$

What are the half-cell reactions associated with this mechanism? The higher order polysulfides (x=8, 6, 4) are soluble in the electrolyte. In contrast, $\mathrm{Li_2S_2}$ and $\mathrm{Li_2S}$ are much less soluble. How could this situation lead to self-discharge in these cells? Identify some options to mitigate this self-discharge.

The half-cell reactions are

$$\mathrm{S_8} + 2\mathrm{Li^+} + 2\mathrm{e^-} \rightarrow \mathrm{Li_2S_8}$$

$$3\mathrm{Li_2S_8} + 2\mathrm{Li^+} + 2\mathrm{e^-} \rightarrow 4\mathrm{Li_2S_6}$$

$$2\mathrm{Li_2S_6} + 2\mathrm{Li^+} + 2\mathrm{e^-} \rightarrow 3\mathrm{Li_2S_4}$$

$$\mathrm{Li_2S_4} + 2\mathrm{Li^+} + 2\mathrm{e^-} \rightarrow 2\mathrm{Li_2S_2}$$

$$2\mathrm{Li_2S_2} + 2\mathrm{Li^+} + 2\mathrm{e^-} \rightarrow 2\mathrm{Li_2S}$$

$\mathrm{Li_2S_8}$, $\mathrm{Li_2S_6}$, and $\mathrm{Li_2S_4}$ are very soluble, whereas $\mathrm{Li_2S_2}$ and $\mathrm{Li_2S}$ are less soluble.

Self discharge occurs when the soluble products diffuse to the negative electrode, where they are oxidized again.

Some means of mitigation include

- change the structure of the porous electrode to trap the polysulfides
- use additives or alternative electrolytes to reduce the solubility of the polysulfides.

The theoretical specific capacity of an electrode was introduced in Section 7.4. Of course to make a full cell, a positive and negative electrode must be combined. If SC^+ and SC^- represent the specific capacity of the positive and negative electrodes, show that the specific capacity of the full cell is given by

$$SC = \frac{SC^+ \times SC^-}{SC^+ + SC^-}.$$

Here it is assumed the capacities in A·h of the two electrodes are the same; that is, the electrodes are matched. If the specific capacity of the positive electrode is 140 mA·h g^{-1} and that of the negative electrode is 300 mA· h g^{-}, what is the specific capacity of the full cell? If the specific capacity of the negative electrode were doubled to 1000 mA· h g^{-1}, how much improvement in the specific capacity of the full cell is achieved?

Use the following notation

g_+ mass of positive material

g_- mass of negative material

SC^+ specific capacity of positive material

SC^- specific capacity of negative material

Use basis of 1 g of positive material, g_+=1

Since the two electrodes are matched to have the same capacity (coulombs)

$$g_+ SC^+ = g_- SC^-$$

Multiply by the theoretical potential to get energy

$$SC = \frac{\text{capacity}}{\text{mass}} = \frac{(1)SC^+}{1 + g_-} = \frac{SC^+}{1 + {SC^+}/{SC^-}} = \frac{SC^+ SC^-}{SC^- + SC^+}$$

b)

$$SC = \frac{(140)(300)}{140 + 300} = 95.5 \text{ mA} \cdot \text{h g}^{-1}$$

c)

$$SC = \frac{(140)(1000)}{140 + 1000} = 123 \text{ mA} \cdot \text{h g}^{-1}$$

An improvement by a factor of 3 in the negative electrode only provides about a 30 % increase in the capacity of the full cell.

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PROBLEM 8-1

$cap = 1512$ [W-h]

$Vc = 3.5$ [V]

$cap_c = 4.5$ [A-h]

$$Nc = \mathbf{Trunc}\left[\frac{cap}{cap_c \cdot Vc}\right] + 1$$

$$m = \frac{Vbatt}{Vc}$$ *cells in series*

$Nc = m \cdot n$

n=1;

number of parallel strings, only integer number possible but mathematically we can treat as a variable

$Vmax = m \cdot Vcharge$

$Vmin = m \cdot Vcutoff$

$Vcharge = 4.1$ [V]

$Vcutoff = 2.75$ [V]

The only option that meets the requirement uses the 4.5 Ah cell in a 97S1P arrangement

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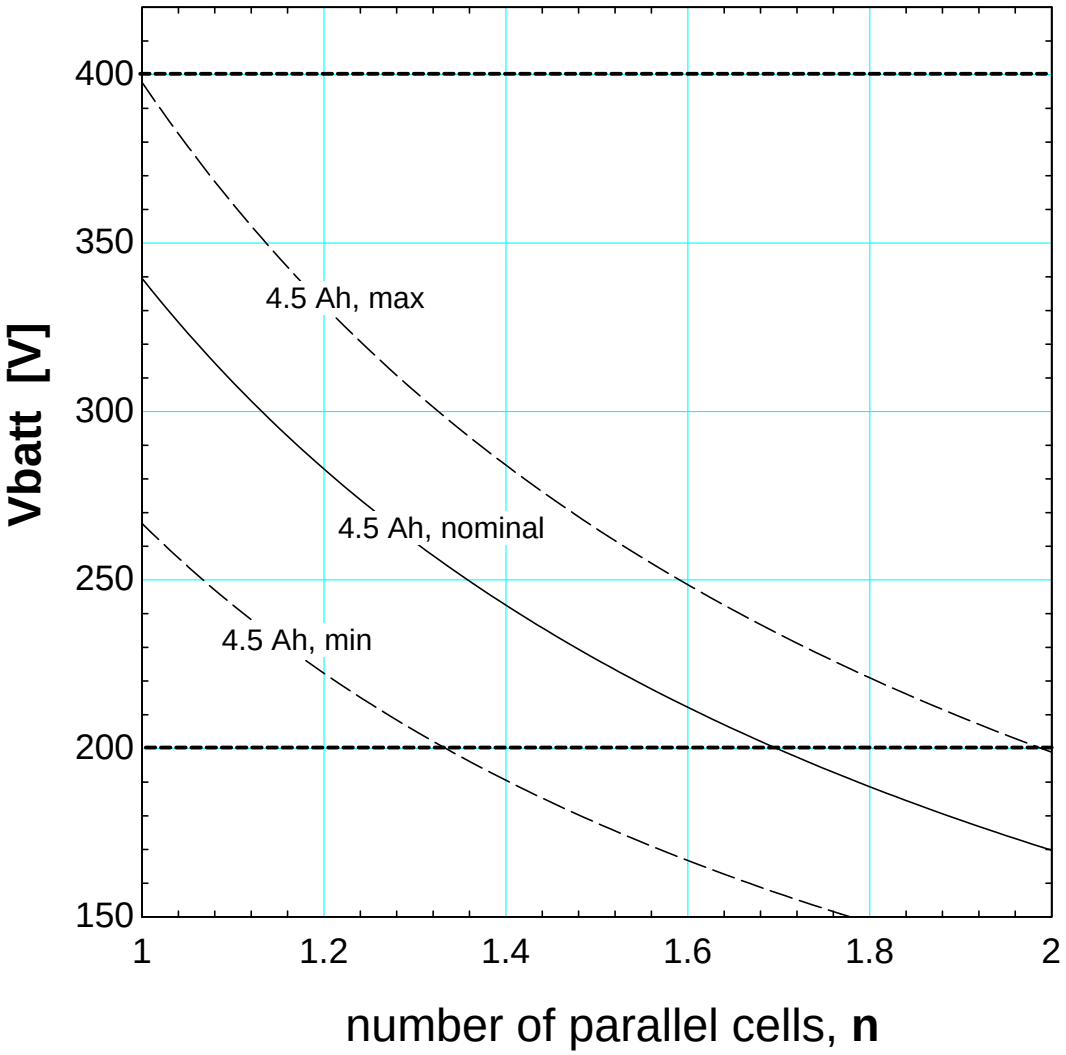

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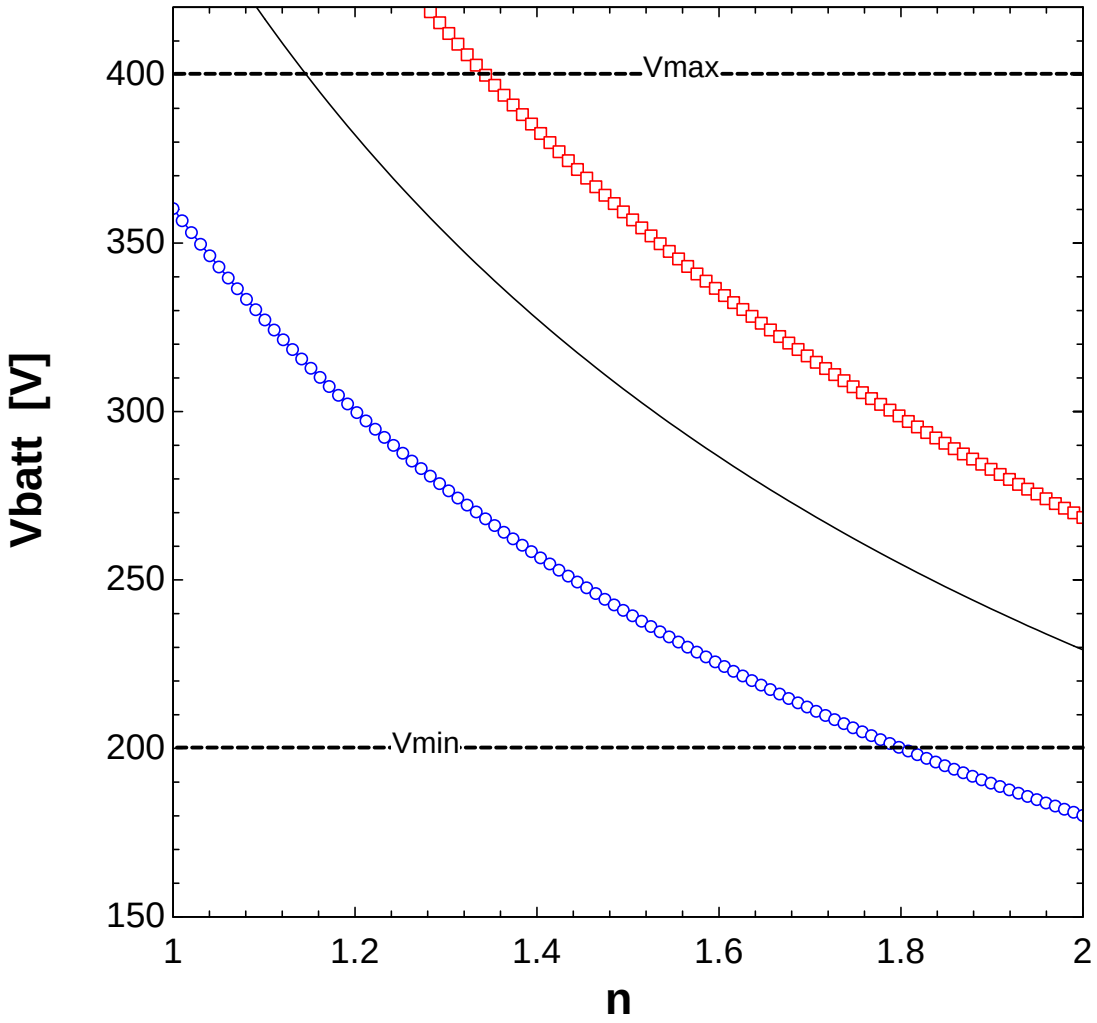

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PROBLEM 8-2

cap = 1512 [W-h] *energy capacity of battery*

Vc = 3.5 [V] *nominal voltage of cell*

Vbatt = 300 [V] *set as firm requirement*

$$Nc = \textbf{Trunc}\left[\frac{cap}{cap_c \cdot Vc}\right] + 1$$

$$m = \textbf{Trunc}\left[\frac{Vbatt}{Vc}\right] + 1$$ *cells in series*

Nc = m · n

n = 1 *number of parallel strings*

Vmax = m · Vcharge

Vmin = m · Vcutoff

Vcharge = 4.1 [V]

Vcutoff = 2.75 [V]

The configuration would be 86S1P, with a capacity of 5.025 Ah

This configuration would be similar to that found in problem 1: 97S1P. Both use a single string of cells. But in this example, the higher cell capacity (5.025 Ah) is preferred because it allows the battery voltage to be roughly centered between the minimum and maximum allowable values.

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cap = 1512 [W-h]
m = 86
Nc = 86
Vc = 3.5 [V]
Vcutoff = 2.75 [V]
Vmin = 236.5 [V]

cap_c = 5.025 [A-h]
n = 1
Vbatt = 300 [V]
Vcharge = 4.1 [V]
Vmax = 352.6 [V]

No unit problems were detected.

Derive equation 8-23 for the maximum power for an ohmically limited cell. What is the expression for maximum power if there is a cutoff potential greater than one half of the open-circuit potential?

For an ohmically limited cell

$$V_{cell} = V_{\text{ocv}} - IR_{\text{int}}$$

and the power is

$$P = IV = I(V_{\text{ocv}} - IR_{\text{int}})$$

The maximum is determined by setting the derivative to zero

$$\frac{dP}{dI} = 0 = V_{\text{ocv}} - 2IR_{\text{int}}$$

so

$$I = \frac{V_{\text{ocv}}}{2R_{\text{int}}}$$

Thus,

$$V_{cell} = U - IR_{\text{int}} = \frac{V_{\text{ocv}}}{2}$$

and

$$P_{max} = IV = \frac{V_{\text{ocv}}^2}{4R_{\text{int}}}$$

If there is a cutoff potential that is greater than $\frac{V_{\text{ocv}}}{2}$, then the power is limited to $V_{cell} = V_{co}$

$$I = \frac{V_{\text{ocv}} - V_{co}}{R_{\text{int}}}$$

and

$$P_{max} = \frac{V_{co}(V_{\text{ocv}} - V_{co})}{R_{\text{int}}}$$

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PROBLEM 8-4

INPUTS

$m = 50$ *series*

$n = 3$ *parallel cells*

$R_{int} = 0.002$ [Ω]

$OCV = 3.1$ [V]

$Vco = 2.75$ [V]

CALCULATIONS

$Nc = m \cdot n$

$Pmax = Nc \cdot OCV \cdot \frac{OCV}{4 \cdot R_{int}}$ *maximum power based--no cut-off potential and no external resistance*

$Pco = Nc \cdot Vco \cdot \left[\frac{OCV - Vco}{R_{int}}\right]$

$P = 0.95 \cdot Pco$ *assumes 5 % loss in power*

Next, consider external resistance

$Rex = Rw \cdot \left[\frac{1 + m}{n}\right]$

$R_{tot} = Rex + \frac{m}{n} \cdot R_{int}$ *resistance of the series parallel connected cells*

$P = m \cdot Vco \cdot m \cdot \left[\frac{OCV - Vco}{R_{tot}}\right]$

$Vcell = m \cdot Vco$

$I = m \cdot \left[\frac{OCV - Vco}{R_{tot}}\right]$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

I = 498.7 [A]	m = 50
n = 3	Nc = 150
OCV = 3.1 [V]	P = 68578 [W]
Pco = 72188 [W]	Pmax = 180188 [W]
Rex = 0.001754 [Ω]	Rw = 0.0001032 [Ω]
R_{int} = 0.002 [Ω]	R_{tot} = 0.03509 [Ω]
Vcell = 137.5 [V]	Vco = 2.75 [V]

No unit problems were detected.

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PROBLEM 8-5

Cellcap = 3.1 [A-h]

Nc = 6831

cap = Nc · Vc · Cellcap *energy capacity of battery*

Vc = 3.6 [V] *nominal voltage of cell*

Vbatt = 355 [V]

$$Nc = \textbf{Trunc}\left[\frac{cap}{cap_c \cdot Vc}\right] + 1$$

$$m = \textbf{Trunc}\left[\frac{Vbatt}{Vc}\right] + 1$$ *cells in series*

Nc = m · n

A battery voltage of 300-400 V is generally desired

355 V, gives a configuration of 99S69P.

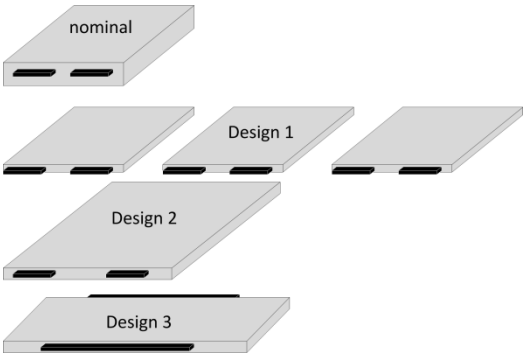
SOLUTION

Unit Settings: SI C kPa kJ mass deg

cap = 76234 [W-h]
Cellcap = 3.1 [A-h]
n = 69
Vbatt = 355 [V]
cap_c = 3.1 [A-h]
m = 99
Nc = 6831
Vc = 3.6 [V]

No unit problems were detected.

The nominal design of a 20 A·h cell is shown on the right. The tabs for current collection are on the same side and the dimensions of the cell ($L \times W \times H$) are 140×100×15 mm. Alternative designs are being considered.



Option	Capacity, A·h	*L*, mm	*W*, mm	tabs
Nominal	20	140	100	narrow, same side
1	6.67	140	100	narrow, same side
2	20	200	140	narrow, same side
3	20	250	120	opposite sides, wide

a. Assuming that the electrodes and current collectors are unchanged and that the thickness of the current collector is small relative to the cell thickness, what are the cell thicknesses of the alternate designs?
b. Discuss the advantages and disadvantages of these alternatives. For option 1, three cells are required to keep the capacity the same. Consider the following in your answer
   i. heat removal from a relatively long stack of the cells under consideration
   ii. uniformity of current density across the planform
   iii. rate capability, resistance of current collectors and tabs

a) To a first approximation, the volumes are all the same.

Option 1, requires three cells

$$t_1 = \frac{140 \times 100 \times 15}{140 \times 100 \times 3} = 5 \text{ mm}$$

Option 2,

$$t_2 = \frac{140 \times 100 \times 15}{140 \times 200} = 7.5 \text{ mm}$$

Option 3,

$$t_1 = \frac{140 \times 100 \times 15}{120 \times 250} = 7.0 \text{ mm}$$

B) Heat removal. Assume cells are placed in a long stack, no heat removal from ends of the stack. Thickness won't affect removal of heat. Therefore, a smaller planform size is an advantage. Also, because the current collectors have a high thermal conductivity, significant heat can be removed through the tabs.

	planform size	tabs
Option 1	—	—
Option 2	×	—
Option 3	×	✓

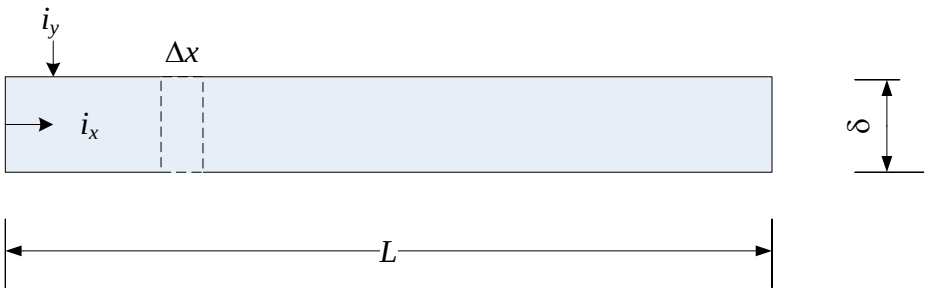
Uniformity of current distribution. Assume thickness of cell sandwich (current collectors and electrodes) is unchanged. Cell is thicker because of more windings or more plates stacked together. Key factors will be the planform size, aspect ratio, and size of the tabs.

	planform size	aspect ratio	tabs
Option 1	—	—	—
Option 2	×	×	—
Option 3	×	×	✓

Rate capability. Depends on the resistance of the current collector and the uniformity of the current distribution

	current distribution	resistance
Option 1	—	—
Option 2	×	×
Option 3	—	✓

L is the characteristic dimension of the electrode, δ the thickness of the current collector and σ its electrical conductivity. The width of the electrode, perpendicular to the section illustrated below, can also be assumed to have a length equal to *L* so that the area of the electrode exposed to the electrolyte is L^2. Show that if the current density over the electrode is constant (i_y), the resistance to current flow in the current collector is $\frac{1}{2\sigma\delta}$. This "average" resistance is defined as the total current that enters the current collector divided by the voltage drop across the current collector. Assume that electrical connection to the current collector is made at *x* = *L*, and treat current flow in the current collector as one dimensional. Under these conditions, $i_x = i_y \frac{x}{\delta}$. How should δ be scaled if it is desired to keep the resistance ratio of the current collector and electrochemical resistance constant? In other words, how should the thickness of the current collector be changed in order to maintain a constant resistance ratio if the size of the electrode, L, were increased or decreased?



$$(\delta L)di_x = Li_y dx$$

integrate

$$\int_0^{i_x} di_x = \frac{i_y}{\delta}\int_0^x dx$$

$$i_x = i_y \frac{x}{\delta}$$

Now apply Ohm's law

$$i_x = -\sigma\frac{d\phi}{dx} = i_y\frac{x}{\delta}$$

$$d\phi = -\frac{1}{\sigma}i_x dx = \frac{i_y}{\sigma\delta}xdx$$

integrate

$$\Delta\phi = \frac{i_y L^2}{2\sigma\delta}$$

The resistance is defined as

$$R_\Omega = \frac{\Delta\phi}{I} = \frac{\frac{i_y L^2}{2\sigma\delta}}{i_y L^2} = \frac{1}{2\sigma\delta}$$

This is the resistance of the current collector, R_{cc}. Thus

$$R_{\mathrm{cc}} \propto \frac{1}{2\sigma\delta}$$

and for charge transfer

$$R_{\mathrm{ct}} \propto \frac{1}{\mathrm{Area}} = \frac{1}{L^2}$$

Keep the ratio $R_{\mathrm{cc}}/R_{\mathrm{ct}}$

$$\mathrm{constant} = \frac{L^2}{2\sigma\delta}$$

If the electrode length, *L*, is doubled, the thickness should be increased by a factor of four.

For current collectors in lithium-ion cells copper foil is used for the negative electrode and aluminum foil for the positive. Often the aluminum foil is about 1.5 times as thick as the copper. Why is this done?

Look at the conductivity of copper and aluminum

$$\sigma_{\mathrm{Cu}} = 58.5 \times 10^{6}\ \mathrm{S\ m^{-1}}$$

$$\sigma_{\mathrm{Al}} = 36.9 \times 10^{6}\ \mathrm{S\ m^{-1}}$$

The ratio of the two is

$$\frac{\sigma_{\mathrm{Cu}}}{\sigma_{\mathrm{Al}}} = \frac{58.5}{36.9} = 1.6$$

Because the conductivity of the aluminum is lower, the thickness of the Al current collector is increased so that the resistances of the current collectors are about the same.

Using data from Figure 8-12, determine charging and discharging resistance of the cell. The answer should be in Ω-m^2. Compare these values with the ohmic resistance of the same cell. Discuss why the values are different.

$$R_{cell}^{d} = \frac{V(t_0) - V(t_1)}{\Delta i} = \frac{3.7 - 3.47}{80} = 2.9\ \text{m}\Omega \cdot \text{m}^{-2}$$

$$R_{cell}^{c} = \frac{3.8 - 3.67}{60} = 2.8\ \text{m}\Omega \cdot \text{m}^{-2}$$

$$R_{\Omega} = \frac{3.7 - 3.56}{80} = 1.7\ \text{m}\Omega \cdot \text{m}^{-2}$$

or

$$R_{\Omega} = \frac{3.77 - 3.67}{60} = 1.7\ \text{m}\Omega \cdot \text{m}^{-2}$$

As expected, the ohmic resistance is lower than the cell resistance, which includes kinetic polarization and concentration polarization. The discharge resistance is slightly higher probably because the change in current density is a bit larger.

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problem 8-11

Δ_{SOC} = 0.8

charge = 119 [A-h]

cap = 125 [A-h]

$$chargecoefficient = \frac{charge}{cap \cdot \Delta_{SOC}}$$

if the rate of charging is increased, then the overpotential at the electrodes also increases. The rate of side reactions will increase. Without further information we're not able to predict whether the desired reaction or side reaction will increase faster. The same situation exists with temperature. Generally, the charge coefficient will be larger.

SOLUTION

Unit Settings: SI C kPa J mass deg

cap = 125 [A-h]
chargecoefficient = 1.19
charge = 119 [A-h]
Δ_{SOC} = 0.8

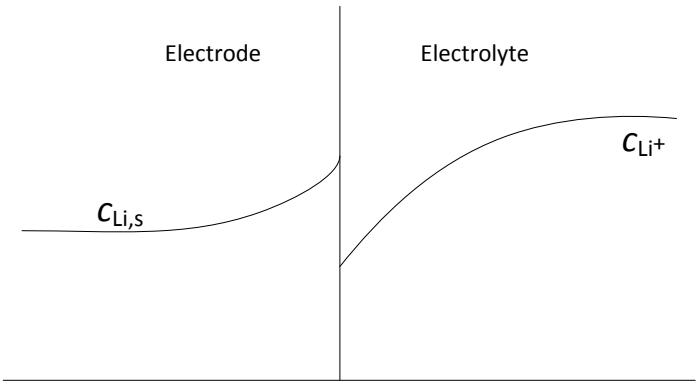
No unit problems were detected.

During charging of a lithium-ion battery, lithium ions are transported to the negative electrode, where they are reduced and then intercalate into the graphite active material. One limitation on the rate of charging is the concentration of lithium at the interface. If the rate is too high, then lithium metal can plate, which is a dangerous situation. This level of lithium is sometimes referred to as the saturation level.

a. Qualitatively sketch the concentration profile of lithium in the electrolyte and in the graphite. How do these profiles change with the rate of charging?

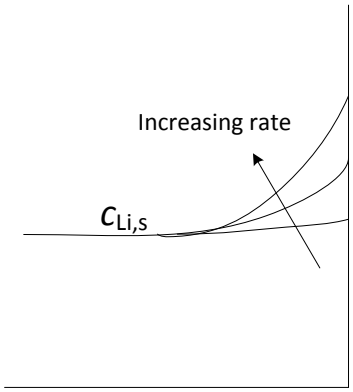
b. Discuss differences that correspond to the following charging protocols: 1) Constant current density of 20 $A \cdot m^{-2}$ until the saturation level of lithium is reached, and 2) Repeated pulses of charging at 25 $A \cdot m^{-2}$ for 3 seconds followed by a lower rate of 5 $A \cdot m^{-2}$ for 1 second.

a)



During charging lithium moves into the negative electrode. Therefore, there is a gradient of concentration in the solid phase. This is shown for a planar geometry in the figure. In the electrolyte, lithium also moves into the electrode. At the interface, the flux is the same, but the concentration and its gradient are different.

b) at higher rates (higher current) the gradients become steeper. For the solid phase



c) On average the current density is the same for both cases

$$\frac{(25 \times 3) + (5 \times 1)}{4} = 20 \text{ A m}^{-2}$$

No change in the time to reach the saturation level of Li. See *J. Electrochem. Soc*., **153**, A533 (2006) for a detailed discussion. More elaborate charging schemes are needed to reduce the charging time.

Lithium-ion batteries have self-discharge rates of 1-2 % per month. If two adjacent cells in a long string connected in series have rates of self-discharge of 1 % and 2 % per month, respectively, and the battery is fully charged each month, how long before the SOCs of these two cells vary by 5%? The rate of self-discharge, however, can be as high as 5% in the first 24 hours. If the initial rates of self-discharge for the two cells are 3 and 5 % respectively, how does the answer change? What role would the battery management system play in this scenario?

a)

$$\Delta \text{SOC} = 0.05 = \frac{0.01}{\text{month}}\Bigg| \frac{t}{}$$

$$t = 5 \text{ months}$$

b)

$$0.05 = \frac{(0.05 - 0.03)}{\text{day}}\Bigg| \frac{t}{}$$

$$t = 2.5 \text{ days}$$

c) The role of the BMS is to monitor the potential of individual cells so that cells are not overcharged and to balance the SOC of during each charge. The cell with a greater rate of self-discharge will be charged more to bring all of the cells to the same SOC.

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PROBLEM 8-14

$ri = 0.002$ [m] *winding shaft diameter*

$\delta = 0.0005$ [m]

$L = 1.8$ [m]

$ro = \sqrt{ri \cdot ri + \delta \cdot \frac{L}{\pi}}$ *outer diameter*

$r = 0.002$ [m]

$\dot{q} = 50000$ [W/m^3] *heat generation rate*

Next, calculate temperature profile in battery

$k_{eff} = 0.15$ [W/m-C] *use value from Todd's paper*

$To = 25$ [C]

$$T = \frac{\dot{q}}{4 \cdot k_{eff}} \cdot [ro \cdot ro - r \cdot r] + To$$

$$\theta = To + \frac{\dot{q}}{4 \cdot k_{eff}} \cdot \left[ro \cdot ro - r \cdot r + 2 \cdot ri \cdot ri \cdot \ln\left(\frac{r}{ro}\right)\right]$$

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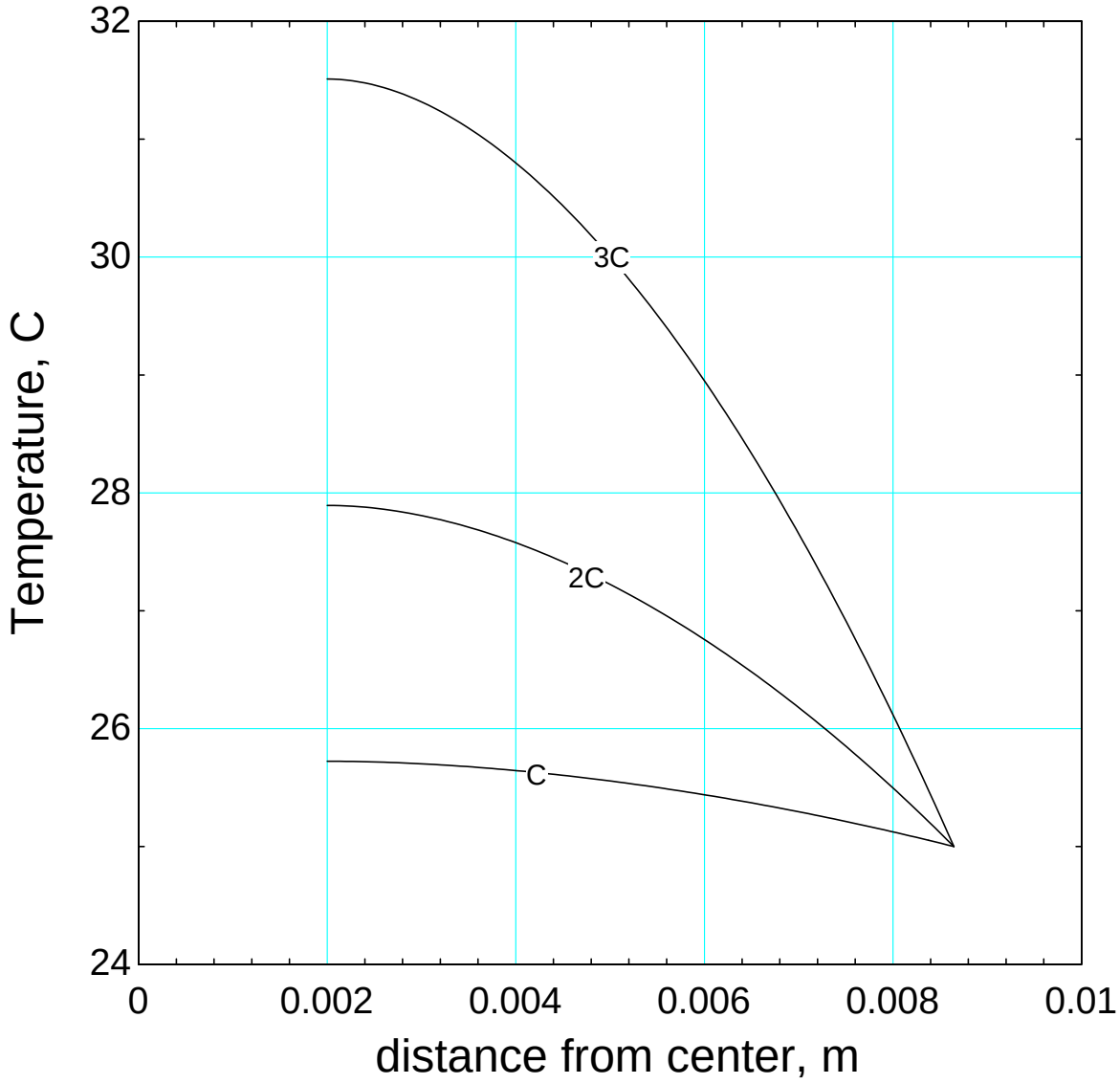

Rather than specifying the temperature at the outside of the cell as was done in Section 8.9, in practice heat is removed by forced convection. What is the appropriate boundary condition? Use h for a heat transfer coefficient and T_∞ for the temperature of the fluid. Solve the differential equation to come up with an equation equivalent to 8-28. In general would liquid or air cooling be more effective? Why?

Starting with Equation 8.27

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{\dot{q}'''}{k_{eff}}=0. \tag{8-27}$$

integrate once

$$r\frac{\partial T}{\partial r}=\frac{-\dot{q}'''}{2k_{eff}}r^2+C_1$$

at $r=r_i$,

$$\frac{\partial T}{\partial r}=0.$$

find the constant

$$C_1=\frac{\dot{q}'''r_i^2}{2k_{eff}}$$

$$r\frac{\partial T}{\partial r}=\frac{\dot{q}'''}{2k_{eff}}r+\frac{C_1}{r}$$

Integrate again,

$$T=\frac{-\dot{q}'''}{4k_{eff}}r^2+C_1\ln r+C_2$$

At the interface between the battery and the cooling fluid, let $T=T_o$; the heat flux across the interface is constant.

$$h(T_o-T_\infty)=-k_{eff}\frac{\partial T}{\partial r}$$

$$\frac{h}{k_{eff}}(T_o-T_\infty)=\frac{\dot{q}'''r_o}{2k_{eff}}-\frac{C_1}{r_o}$$

rearrange

$$T_o=\frac{k_{eff}}{h}\left[\frac{\dot{q}'''r_o}{2k_{eff}}-\frac{C_1}{r_o}\right]+T_\infty$$

$$T_o=\frac{k_{eff}}{h}\left[\frac{\dot{q}'''r_o}{2k_{eff}}-\frac{\dot{q}'''r_i^2}{2k_{eff}r_o}\right]+T_\infty$$

$$T_o=\frac{\dot{q}'''r_o}{2h}\left[1-\frac{r_i^2}{r_o^2}\right]+T_\infty$$

Combine with previous solution, Equation 8.28

$$T = T_\infty + \frac{\dot{q}'''}{4k_{eff}}\left[(r_o^2 - r^2) + 2r_i^2 \ln\frac{r}{r_o}\right] + \frac{\dot{q}'''r_o}{2h}\left[1 - \frac{r_i^2}{r_o^2}\right]$$

The analysis in Section 8.9 is for a cylindrical cell. Develop a similar analysis for a prismatic cell. Assume that all the heat is removed from the top and bottom of the cell (i.e., assume no heat loss from the sides). Furthermore, heat is removed from the bottom of the cell using convection through a cold plate (h_c, T_c) and from the top to ambient, also by convection (h_a, T_a).

Write equation 8.26 for a one dimensional problem in Cartesian coordinates

$$\frac{d^2T}{dx^2} = \frac{-\dot{q}'''}{k_{eff}}.$$

integrate

$$T = \frac{-\dot{q}'''}{2k_{eff}}x^2 + C_1x + C_2$$

Find solution in terms of surface temperatures: boundary conditions:

$$x = 0; \quad T = T_o.$$
$$x = L; \quad T = T_L.$$

find the constants

$$C_2 = T_o$$

$$C_1 = \frac{(T_L - T_o)}{L} + \frac{\dot{q}'''_L}{2k_{eff}}$$

Match heat flux at the ends.

x=0 $$-k_{eff}\frac{dT}{dx} = h_c(T_c - T_o)$$

therefore

$$\frac{(T_L - T_o)}{L} + \frac{\dot{q}'''_L}{2k_{eff}} = \frac{h_c}{k_{eff}}(T_o - T_c) \qquad (1)$$

and at *x*=*L*

$$k_{eff}\frac{dT}{dx} = h_a(T_L - T_a)$$

$$\frac{k_{eff}(T_L - T_o)}{L} - \frac{\dot{q}'''_L}{2} = h_a(T_L - T_a) \qquad (2)$$

We have two equations (1 and 2) in two unknowns, T_o and T_L. Rather than solving algebraically, this is done numerically with EES.

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$k1 = 238$ [W/m-K]

$k2 = 1.5$ [W/m-K]

$k3 = 398$ [W/m-K]

$k4 = 1$ [W/m-K]

$k5 = 0.33$ [W/m-K]

$t1 = 0.000045$ [m]

$t2 = 0.000066$ [m]

$t3 = 0.000032$ [m]

$t4 = 0.000096$ [m]

$t5 = 0.00005$ [m]

$$k_{parallel} = \frac{t1 \cdot k1 + t2 \cdot k2 + t3 \cdot k3 + t4 \cdot k4 + t5 \cdot k5}{t1 + t2 + t3 + t4 + t5}$$

$$k_{perp} = \frac{t1 + t2 + t3 + t4 + t5}{\frac{t1}{k1} + \frac{t2}{k2} + \frac{t3}{k3} + \frac{t4}{k4} + \frac{t5}{k5}}$$

the effective conductivity in the plane of the electrode is almost 100 times larger. The problem only gets worse if multiple electrodes are stacked or wound together. This means that it is very difficult to remove heat in the direction that goes through the separator. Heat removal in the plane of the current collector can be an effective means of cooling

SOLUTION

Unit Settings: SI C kPa J mass deg

$k1 = 238$ [W/m-K]
$k2 = 1.5$ [W/m-K]
$k3 = 398$ [W/m-K]
$k4 = 1$ [W/m-K]
$k5 = 0.33$ [W/m-K]
$k_{parallel} = 81.86$ [W/m-K]
$k_{perp} = 0.9905$ [W/m-K]
$t1 = 0.000045$ [m]
$t2 = 0.000066$ [m]
$t3 = 0.000032$ [m]
$t4 = 0.000096$ [m]
$t5 = 0.00005$ [m]

No unit problems were detected.

a. With greater current density, the SOC changes more quickly. Because the equilibrium potential changes with SOC, this causes current to shift away from the tab region. This is negative feedback.
b. An increase in temperature causes the electrical conductivity to increase and also for the kinetics to improve. Both of these lead to reduced polarization and therefore, greater local current density. The increase in current density results in greater heat generation. This is positive feedback. There is an important mitigating effect. As described above the SOC changes reduce the current density, shifting current away from the hot spot.
c. The voltage is held constant during the float charge. The exothermic reaction can cause the temperature to increase. The higher temperature increases the rate of oxygen evolution and recombination, further increasing the temperature of the cell (positive feedback). If heat removal is not efficient (negative feedback), then the temperature can increase rapidly—thermal runaway.

a. C-rate 60/2=30 C

b. Power is C-rate times capacity in kW-h

Power=30x50kW=1.5 MW

c. Cells with thin electrodes will have higher power capability, but because the mass of the current collectors, separator, and can don't scale with electrode thickness, these cells would have very low energy density. Furthermore, it is more difficult to remove heat and keep ohmic losses in the current collectors and tabs small for large cells.

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PROBLEM 8-20

stack in coin cell

dimension and mechanical data

ds = 0.014 [m]

$$A = \pi \cdot ds \cdot \frac{ds}{4}$$

hsa = 0.0005 [m] *thickness of anode spacer*

Ysa = 2.1×10^{11} [Pa] *Youngs modulus for anode spacer, steel*

ha = 0.00007 [m] *thickness of anode*

Ya = 1.5×10^{10} [Pa] *Youngs modulus for anode , carbon*

hs = 0.000025 [m] *thickness of separator*

Ys = 1×10^{9} [Pa] *Youngs modulus for separator, polymer*

hc = 0.00007 [m] *thickness of cathode*

Yc = 7×10^{10} [Pa] *Youngs modulus for cathode , metal oxide*

hsc = 0.0005 [m] *thickness of cathode spacer*

Ysc = 2.1×10^{11} [Pa] *Youngs modulus for cathode spacer , steel*

hsp = 0.002 [m] *thickness of uncompressed spring*

L = hsa + ha + hc + hsc + hsp *uncompressed thickness of sandwich*

Lc = 0.0024 [m] *compressed thickness*

$$L - Lc = \sigma \cdot \left[\frac{hsa}{Ysa} + \frac{ha}{Ya} + \frac{hs}{Ys} + \frac{hc}{Yc} + \frac{hsc}{Ysc} + \frac{A}{Kmin} \right]$$

Kmin = 120000 [Pa-m] *value for cone washer*

Kdim = 3

Do = 0.015 [m]

Di = 0.01 [m]

$$Dm = \frac{Do + Di}{2}$$

$$\mu = \frac{Do - Di}{Do + Di}$$

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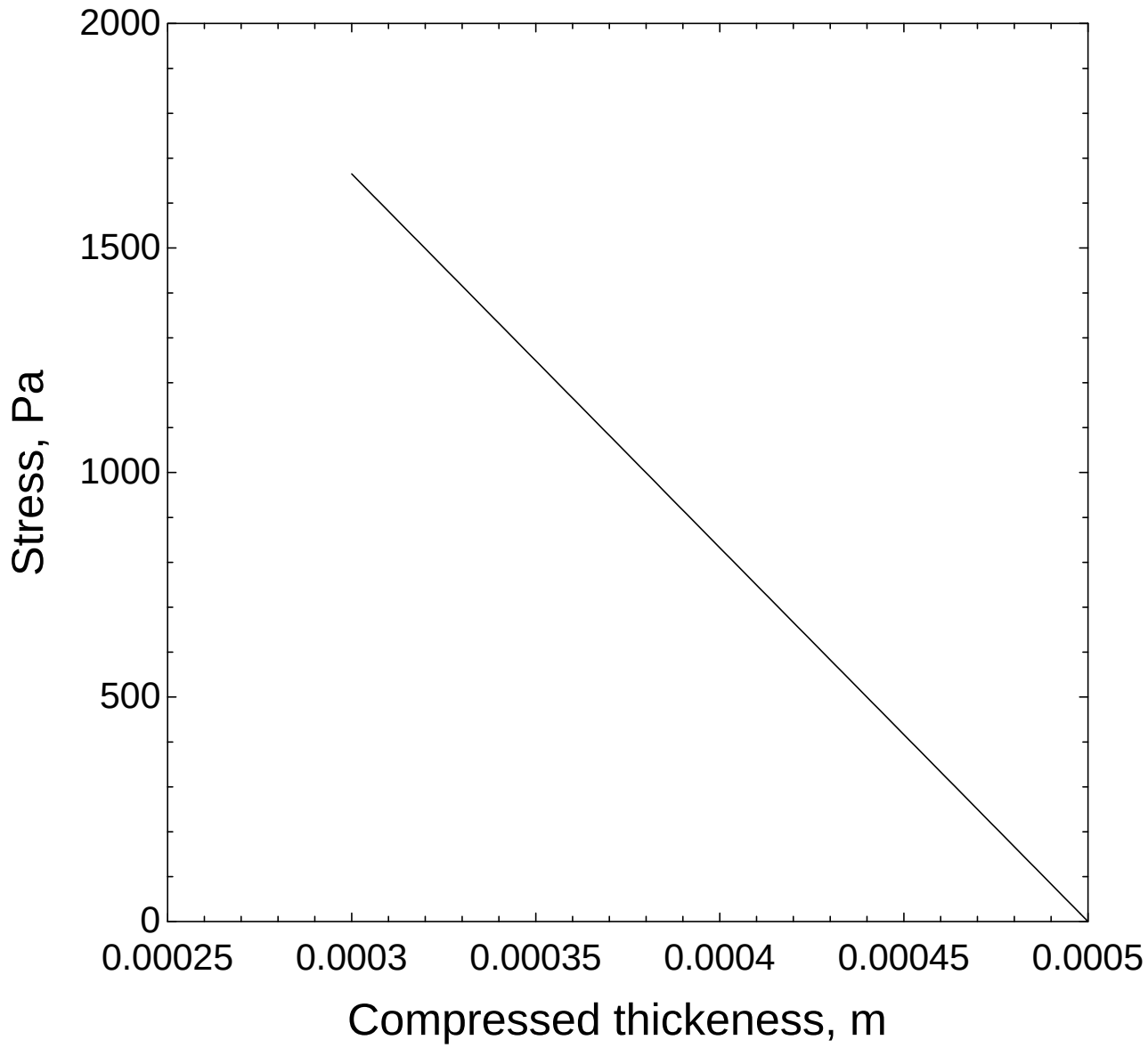
$E = 2 \times 10^{11}$ [Pa]

t = 0.0001 [m]

*Kdim=Kmin*Dm^2/E/t^3*

assuming a wave washer



Derive Equation 8-29. (Hint: how might you express the volume of the wound and unwound cell?)

The volume of the winding is expressed as

$$LW\delta = \pi W(r^2 - r_i^2)$$

rearrange

$$\frac{L\delta}{\pi} = r^2 - r_i^2$$

and

$$\frac{L\delta}{\pi} = r^2 - r_i^2$$

$$r = \sqrt{r_i^2 + \frac{L\delta}{\pi}}$$

Calculate the voltage efficiency, η_V^{fc}, for a fuel cell operating at 0.65 V at standard conditions. The product water is a liquid, the oxidant is air, and the following fuels are used.

a. Methane, CH_4
b. Liquid methanol, CH_3OH
c. Hydrogen, H_2
d. Liquid formic acid, HCOOH

$$\eta_V^{fc} = \frac{V}{U}$$

because problem states that the fuel cell is operating at standard conditions, $U = U^{\theta}$

$$\eta_V^{fc} = \frac{V}{U^{\theta}} = \frac{VnF}{-\Delta G_{Rx}^{o}}$$

a) Methane

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O_{(liq)}$$

Using data from Appendix C

$$\Delta G_{Rx}^{o} = (-394.359) + 2(-237.129) - (-50.5) = -818.1 \text{ kJ mol}^{-1}$$

n=8,

$$\eta_V^{fc} = \frac{VnF}{-\Delta G_{Rx}^{o}} = \frac{(0.65)(8)(96485)}{818{,}100} = 0.61$$

Follow similar process for methanol, hydrogen, and formic acid

	n	U^{θ}	η_V^{fc}
methanol	6	1.21	0.54
hydrogen	2	1.229	0.53
formic acid	2	1.40	0.46

In the development of low-temperature fuel cells, many electrolytes were explored. For a liquid acid type of electrolyte, the phosphoric acid fuel cell was commercialized. However, because of the adsorption of phosphate ions that blocks the access of oxygen, the reduction of oxygen is actually faster in sulfuric acid than it is in phosphoric acid. Given this, discuss possible reasons why phosphoric acid was selected over sulfuric acid for development. Hint: think about the properties of the electrolyte that are important for fuel-cell applications.

There are many requirements for an electrolyte: high conductivity and good kinetics for oxygen reduction are just two. When selecting an electrolyte for any electrochemical process, it must be stable. For the fuel cell, the electrolyte must be stable under both oxidizing and reducing conditions. In contrast to H_3PO_4, sulfuric acid is not stable at the low potentials of the hydrogen electrode. H_2SO_4, particularly at high concentrations, is reduced to form SO_2.

The electrolyte for a molten carbonate fuel cell is a liquid salt mixture of lithium and potassium carbonate (Li_2CO_3 and K_2CO_3). Suggest the electrode reactions for molten carbonate chemistry. The reactants are hydrogen and oxygen, as is common for fuel cells. In addition, carbon dioxide is consumed at the cathode and produced at the anode. How might these high-temperature cells be designed so that the anode and cathode do not short out and so that an effective triple phase boundary is achieved? Discuss the importance of managing gaseous CO_2 in these cells.

The overall reaction is unchanged

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$$

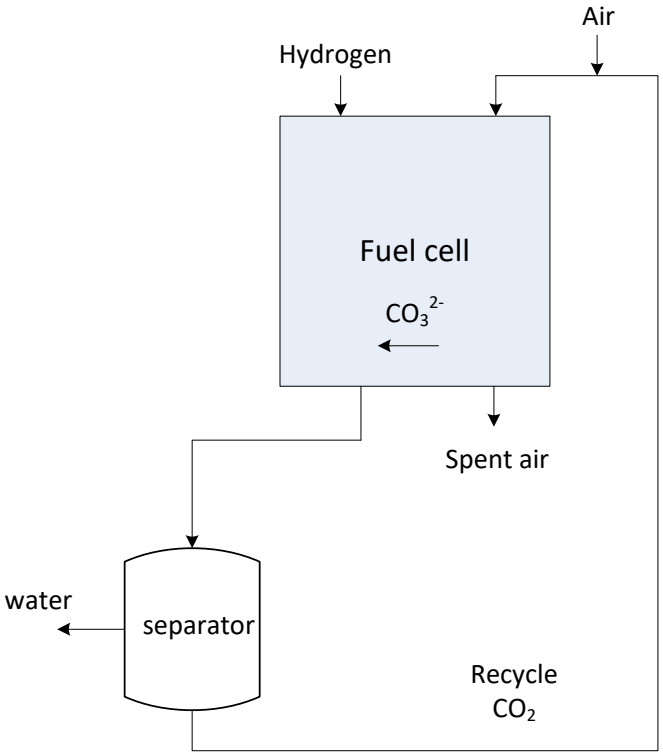
at the cathode

$$CO_2 + \frac{1}{2}O_2 + 2e^- \leftrightarrow CO_3^{2-}$$

and, at the anode

$$CO_3^{2-} + H_2 + +2e^- \leftrightarrow CO_2 + H_2O + 2e^-$$

Carbon dioxide is produced at the anode and consumed at the cathode. CO_2 is recycled to operate the fuel cells—otherwise you would need to supply carbon dioxide to the cathode from another source. A simplified diagram is shown, but in practice the recycle, separation, and balancing CO_2 is a major complication in the operation of a molten carbonate fuel cell.



Basic cell sandwich is the same: anode-separator-cathode. Because of the high temperature of operation, a porous ceramic material is used. The separator prevents the two electrodes from coming into direct contact. The pores of the separator must be completely filled with electrolyte to prevent the gases from crossing from one electrode to the other. The two electrodes are also porous, but only partially filled. By controlling the pore sizes (separator small, electrolyte large) and limiting the amount of electrolyte, the electrodes will only be partially filled so that gas access is allowed.

The performance curves in the figure can be fit with a theoretical curve (*J. Electrochem. Soc.*, **152**, A1290 (1985)). The fitting parameters are shown below. Focus on just two parameters, j_d and R_{int} . What do these parameters represent, and how do their values impact the shape of the performance curves? Discuss the physical changes that were likely made to the cell to achieve the observed changes in performance.

$$V = U - \eta_c - R_{\text{int}} i$$

$$\frac{\eta_c}{b} = \left(1 + \frac{i/j}{1 + i/j} \right) \ln \frac{i}{j} - \ln k - \ln\left(1 - \frac{i}{j_D} \right)$$

Curve	U [V]	b [V]	j [A·m^{-2}]	j_D [A·m^{-2}]	-ln(k)	R_{int} [μΩ·m^2]
1	1.05	0.026	2772	9273	10.18	11.0
2	1.05	0.026	1014	14066	10.72	10.2
3	1.05	0.026	1014	17023	11.01	8.0
4	1.05	0.026	1014	28381	7.0	6.8

The main effects observed are

1) Reduced resistance. In the linear portion of the polarization curve, the magnitude of the slope is lower. This is also seen with the fixed resistance value R_{int}. These values decrease with curves 1-2-3-4. The most likely physical change that causes the reduction in resistance is using a thinner separator

$$R_{int} \approx \frac{L_s}{\kappa_{eff}}$$

Other possible causes are

- more conductive electrolyte, or less tortuous path through separator
- reduced contact resistance
- thinner or more conductive gas diffusion layer or bipolar plate

2) The second dramatic change is in j_d, which corresponds to a limiting current. Mass-transfer resistance is lower and the limiting current is greater

$$j_{d4} > j_{d3} > j_{d2} > j_{d1}$$

Likely physical changes would include

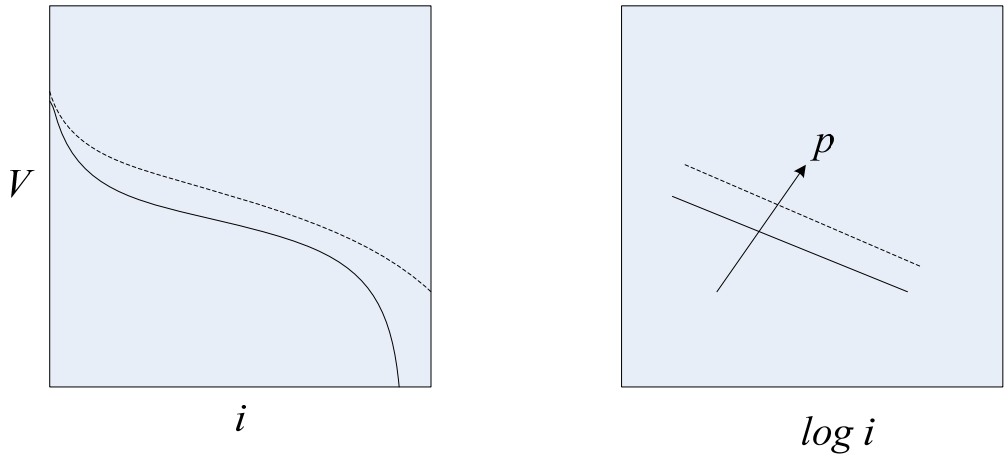
- modifications to the flow-field design
- thinner gas diffusion layer
- better water management (production of liquid water can flood the cell)

Shown are polarization data for a PEM fuel cell operating on hydrogen and air at 70 °C and atmospheric pressure. Also shown is the Tafel plot, where ohmic and anodic polarizations have been removed. By means of a sketch, show how these plots would change under the following conditions:

a. The pressure is raised to 300 kPa
b. The oxidant is changed to pure oxygen in place of air
c. The platinum loading of the cathode catalyst (mg Pt cm^{-2}) is doubled.

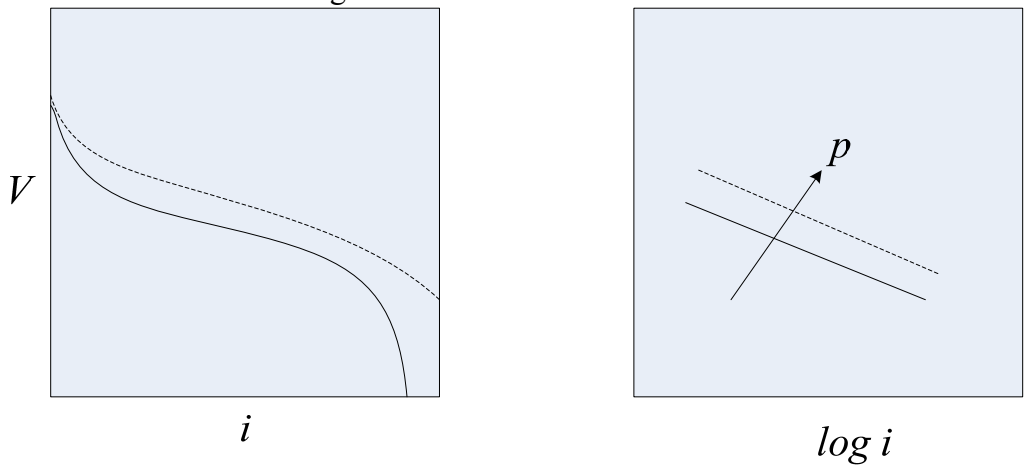
a) Raise pressure by 300 kPa:

- increasing the partial pressure of hydrogen and oxygen will improve the thermodynamic value for H_2 and the kinetic losses for the cathode (the ORR reaction is so sluggish in acid at low temperature, that equilibrium potential are not observed)
- no impact on ohmic losses
- lower mass transfer resistance, resulting in a higher limiting current.



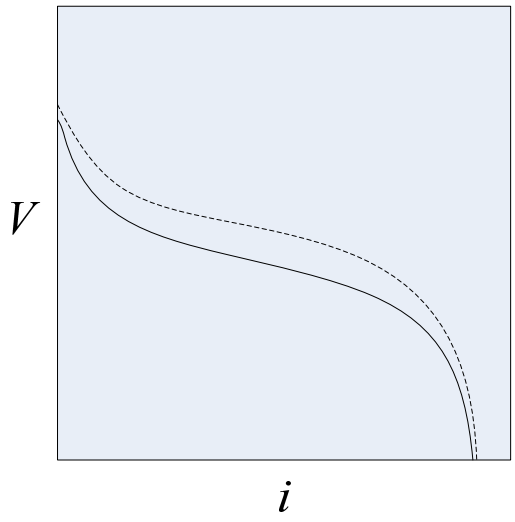
b) replace air with oxygen

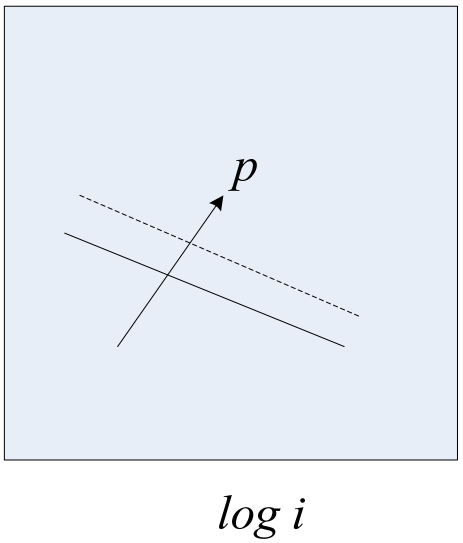
- decrease in kinetic polarization at the cathode
- no change in ohmic losses
- increase in limiting current at the cathode



c) Increase loading of catalyst at the cathode

- improved kinetics at the cathode
- no change in ohmic losses
- no change in limiting current





A polarization curve for a molten carbonate fuel cell is shown in the figure. The temperature is 650 °C, and the electrolyte is a eutectic mixture of lithium and potassium carbonate. Discuss the polarization curve in terms of the four principal factors that influence the shape and magnitude of the curve.

Open-circuit potential

$$U = U^o(650) + \frac{RT}{2F}\ln\frac{a_{\mathrm{H2}}a_{\mathrm{O2}}^{0.5}}{a_{\mathrm{H2O}}}$$

From Figure 9.4,

$$U^o(650) = 1.02\ \mathrm{V}$$

also

$$a_{\mathrm{H2}} = 0.75\left(\frac{200}{100}\right)$$

$$a_{\mathrm{O2}} = 0.19\left(\frac{200}{100}\right)$$

$$a_{\mathrm{H2}} = 0.06\left(\frac{200}{100}\right)$$

$$U = U^o(650) + \frac{RT}{2F}\ln\frac{a_{\mathrm{H2}}a_{\mathrm{O2}}^{0.5}}{a_{\mathrm{H2O}}} = 1.11\ \mathrm{V}$$

This value is the same as the open-circuit potential on the polarization curve.

At the highest current densities shown, we don't see any mass transfer limitations. The cell appears to be entirely ohmically limited (linear decrease in potential with current). There is no apparent kinetic region either, presumably at 650 °C the kinetics are fast enough to keep the kinetic polarization low.

A series of polarization curves at different temperatures for a direct methanol fuel cell are shown in the figure. This cell uses a Nafion separator. It is suggested that Nafion is permeable to methanol. Could this explain why the open-circuit potential is so low? What information about the cell can be inferred from these data specifically?

In acid at low temperatures (32-70 °C) the oxidation of methanol is slow even in the presence of a precious metal catalyst. Thus, the DMFC has two electrodes with high overpotentials. Even without a large amount of methanol permeation across the separator, we would expect a low OCV relative to the thermodynamic value. Any methanol that diffuses across the membrane separator and reaches the cathode will reaction with oxygen. This crossover of methanol is a chemical short. In effect, even with no external current flow, the cathode is polarized.

Yes, methanol crossover can explain the low open-circuit potential. The OCV increases with increasing temperature because the reaction kinetics are improved.

Also evident is a decrease in resistance with temperature (look at the slope of the polarization curve in the mid-current range). This also makes sense because we expect the conductivity of the Nafion to increase with temperature resulting in a lower resistance.

Finally, we note that there is a region of mass-transfer control, which also improves with increasing temperature.

A series of anode supported SOFCs were tested at 800 °C. The only parameter that was changed was the thickness of the electrolyte. Data for the cell resistance measured with current interruption are shown in the table. Determine the conductivity of the YSZ electrolyte and the fraction of the resistance that can be ascribed to the interlayers, current collectors and contact resistances combined.

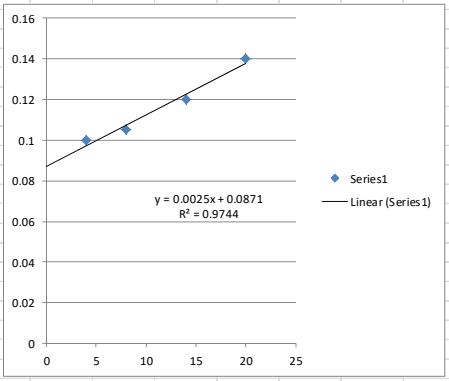
Plot the data and fit to a line

$$R_{elec} = \frac{L}{\kappa}$$

$$\text{slope} = \frac{R_{elec}}{L} = \frac{1}{\kappa}$$

$$\frac{0.0025\ \Omega \cdot \text{cm}^2}{\mu\text{m}} \left| \frac{10^4 \mu\text{m}}{\text{cm}} \right. = 25\ \Omega \cdot \text{cm}$$

electrolyte thickness, μm	ohmic resistance, ohm-cm2
4	0.1
8	0.105
14	0.12
20	0.14

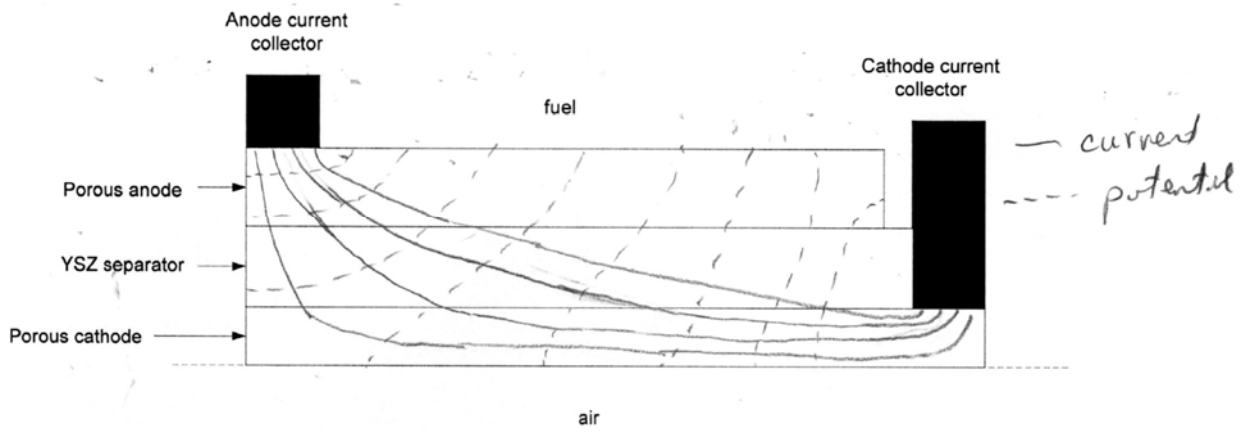


$$\kappa = \frac{1}{\text{slope}} = 0.04\ \text{S cm}^{-1}$$

The intercept is $0.0871\ \Omega \cdot \text{cm}^2$, at 14 μm

$$\text{fraction} = \frac{0.0871}{0.12} = 0.73$$

The tubular configuration is the most developed design for the solid-oxide fuel cell. This design is shown in the figure. Air flows through the center and fuel flows over the outside. The separator is YSZ (yttria stabilized zirconia), an oxygen ion (O^{2-}) conductor. What is the direction of current flow in the cell? How is the current carried in the cell? Sketch the potential and current distributions in the cell. Use the approximate schematic shown in the figure, where one half of the tube has been flattened out. Why is the performance (current–potential relationship) of the tubular design much lower than that of planar designs?



Isopotential lines should be normal to any insulators and parallel to conductors. The current flows normal to the isopotential lines.

Because the current path in the tubular design is much longer than in planar geometries, there is much greater ohmic resistance in the tubular design. Whereas planar geometries are able to achieve high current densities at good efficiencies, the tubular design is limited to low current densities.

On the other hand, the advantages of the tubular design is that it is less susceptible to thermal stress, allows for easier sealing, and tolerates a much greater number of thermal cycles (start-ups and shut-downs).

A proton-exchange membrane (PEM) fuel cell is fabricated with a separator that is 100 μm thick and has a conductivity of 5 S m^{-1}. The cell is operating on hydrogen and air.

a) If the open-circuit potential is 0.96 V, which corresponds to 20 A·m^{-2} of cross-over current calculate the maximum power per unit area if only ohmic losses in the separator are considered.

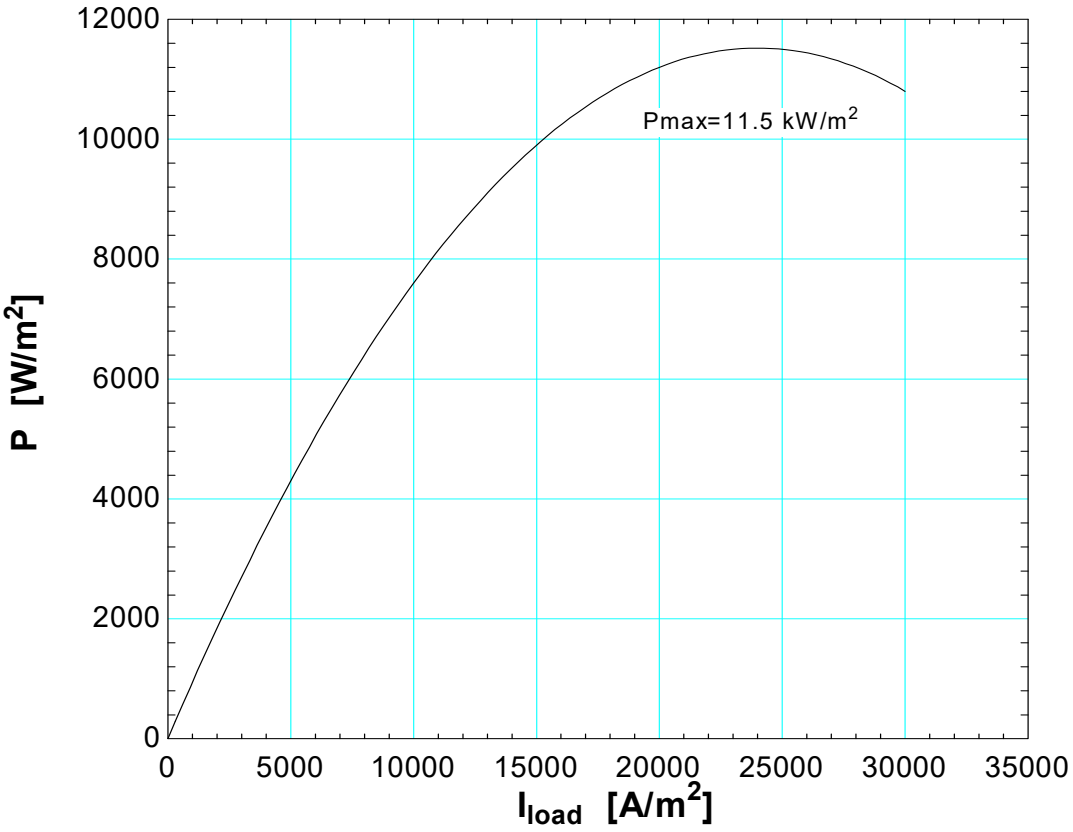
b) For the ohmically limited cell in part (a), sketch the current–voltage relationship. On the same graph compare the performance of a cell that includes kinetic- and mass-transfer polarization. Explain the curve.

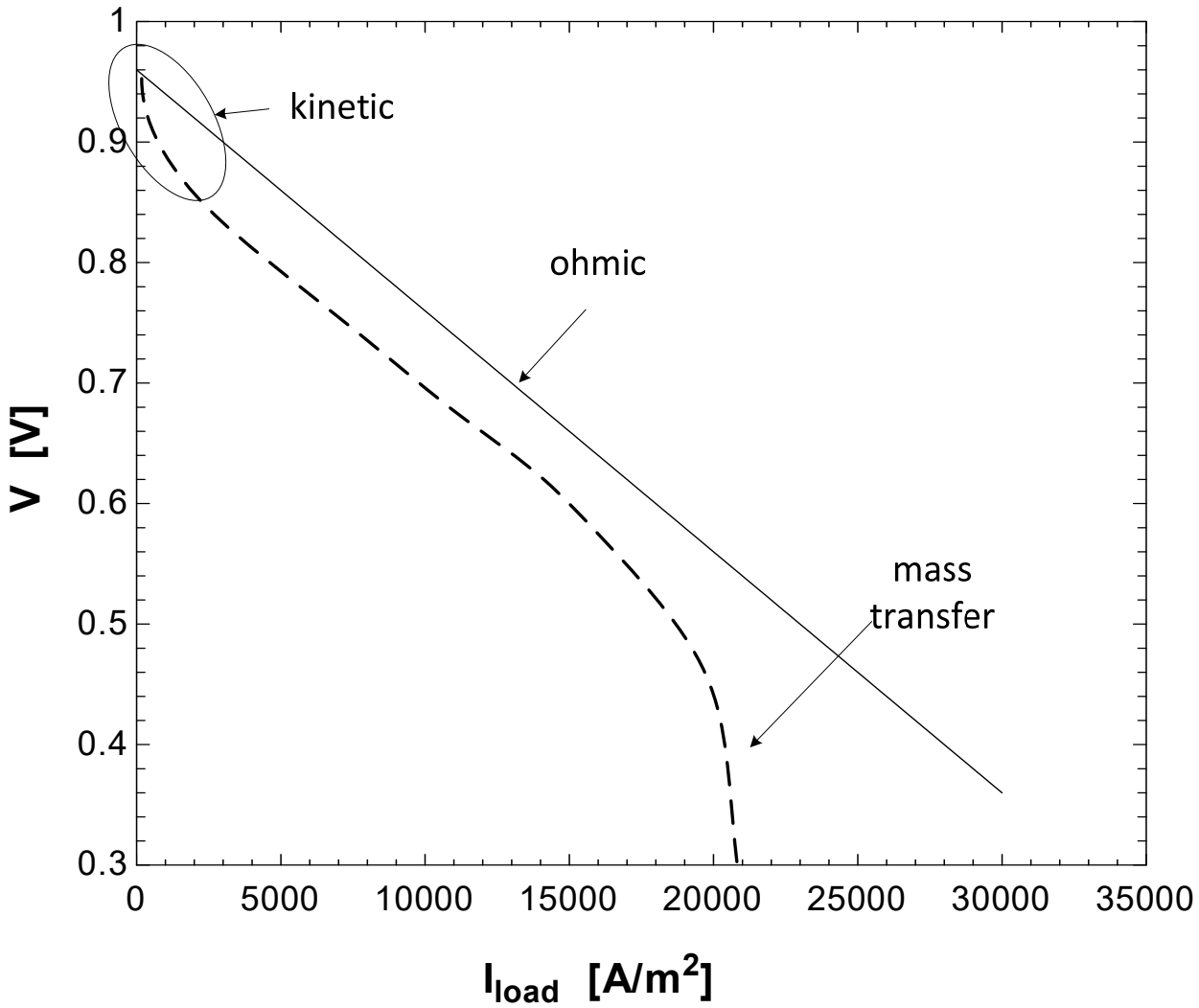
a)

$$V_{OCV} = U - i_{xo}\frac{L}{\kappa}$$

$$V = U - (i_{load} + i_{xo})\frac{L}{\kappa}$$

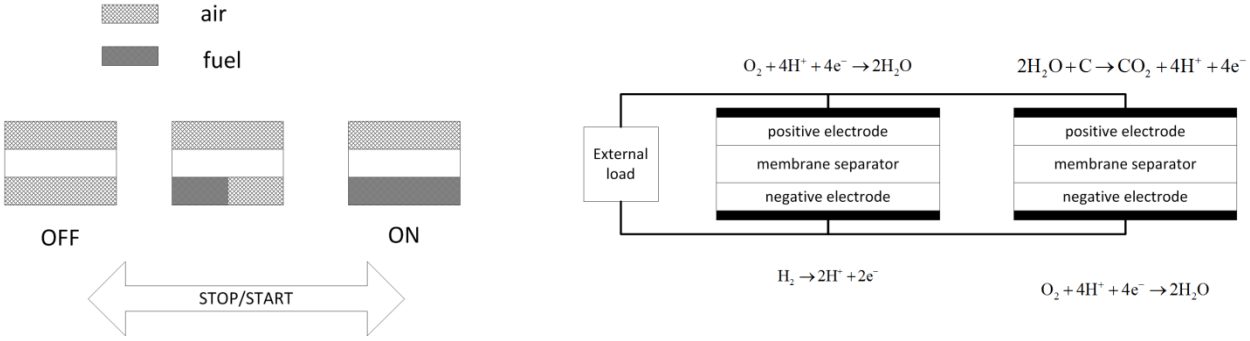
From plot, the maximum areal power density is 11.5 kW m^{-2}.





The resistance is unchanged; therefore, the slope in the mid-current region is the same. However, because of kinetic polarization, the potential of the cell diverges from the ohmically limited cell at low current density (kinetic region). Also, at high current densities, a limiting current is reached.

After a prolonged shut-down of a PEM FC, both the anode and the cathode will contain air. During start-up, a front of hydrogen displaces the air in the fuel channels. This condition is illustrated in the figure and was first reported by Reiser *et al., Electrochem. Solid State Lett.,* **8**, A273 (2005). This situation is clearly transient and 2D in nature. Nonetheless, we can gain insight by examining a one-dimensional, steady-state analog, shown in the figure.



The two cells are electrically connected in parallel to an external load. Cell (1) has air and fuel provided normally, and the second cell (2) has air on both electrodes. At the positive electrode of the cell (2) oxygen evolution or carbon corrosion can occur. At the negative electrode of cell (2) we can expect oxygen reduction. For any reasonable potential, the current through the second cell will be small and we may assume that the solution potential, Φ_2, is nearly constant between the anode and cathode of that cell. The anodic and cathodic currents for cell (2) must be equal to each other. Assuming Tafel kinetics for oxygen reduction and carbon corrosion, and assuming the kinetics for hydrogen oxidation to be fast, estimate the overpotential for carbon corrosion in cell (2) as a function of the measured potential of the cell V_c.

For the cell on the right, the anodic reaction is the oxidation of carbon

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

the cathodic reaction on the other electrode is oxygen reduction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The magnitude of these two currents (oxidation of C and reduction of oxygen must be equal. Assuming Tafel kinetics

$$i_o^1 \exp\left\{\frac{\alpha_a F}{RT}\left(\phi_1^+ - \phi_2 - U_1^\theta\right)\right\} = i_o^2 \exp\left\{\frac{-\alpha_c F}{RT}\left(\phi_1^- - \phi_2 - U_2^\theta\right)\right\}$$

where

i_o^1 exchange current density for C oxidation

i_o^2 exchange current density for oxygen reduction

ϕ_1^+ metal potential of positive electrode

ϕ_1^- metal potential of negative electrode

U_1^θ standard potential for carbon corrosion, 0.207 V

U_2^θ standard potential for oxygen reduction, 1.229 V

ϕ_2 solution potential adjacent to respective electrode

If the current is small, the potential in the electrolyte doesn't change much. Therefore, we assume that the solution potential is the same in the two Tafel expression provided above.

The equation above is rearranged to solve for the solution potential, ϕ_2

$$\phi_2 = \frac{RT}{F(\alpha_a + \alpha_c)} \ln\left(\frac{i_o^1}{i_o^2}\right) - \frac{\left(\alpha_a U_1^\theta + \alpha_c U_2^\theta\right)}{(\alpha_a + \alpha_c)} + \frac{(\alpha_a \phi_1^+ + \alpha_c \phi_1^-)}{(\alpha_a + \alpha_c)}$$

Since the two cell are connected in parallel, ϕ_1^-, the metal potential is the same as in cell 1, which is the hydrogen electrode. We can set this to zero, $\phi_1^- = 0$. Further, $\phi_1^+ = V_{cell}$. Thus,

$$\phi_2 = \frac{RT}{F(\alpha_a + \alpha_c)} \ln\left(\frac{i_o^1}{i_o^2}\right) - \frac{\left(\alpha_a U_1^\theta + \alpha_c U_2^\theta\right)}{(\alpha_a + \alpha_c)} + \frac{V_{cell}\alpha_a}{(\alpha_a + \alpha_c)}$$

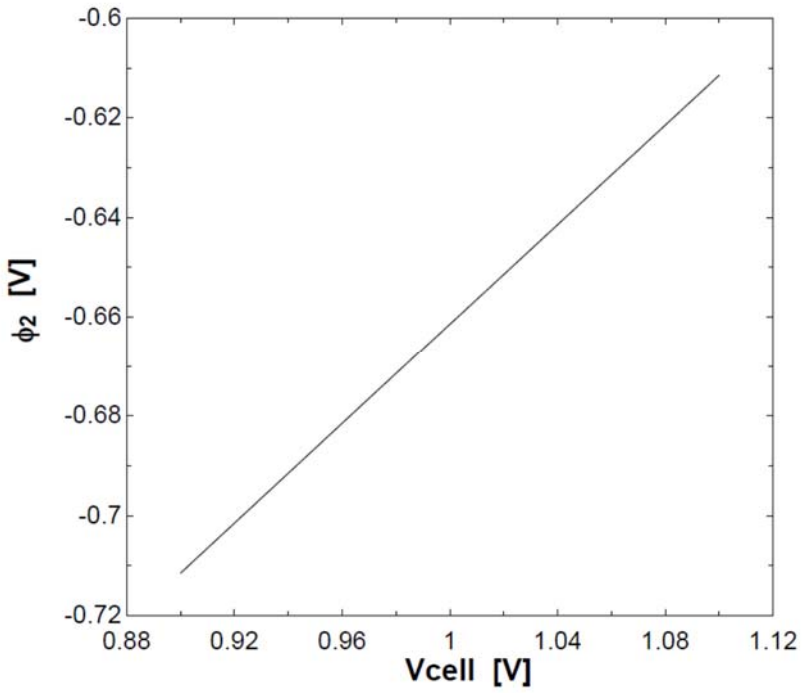
with $\alpha_a = \alpha_c = 1$,

$i_o^1 = 10^{-24}$ A m^{-2},

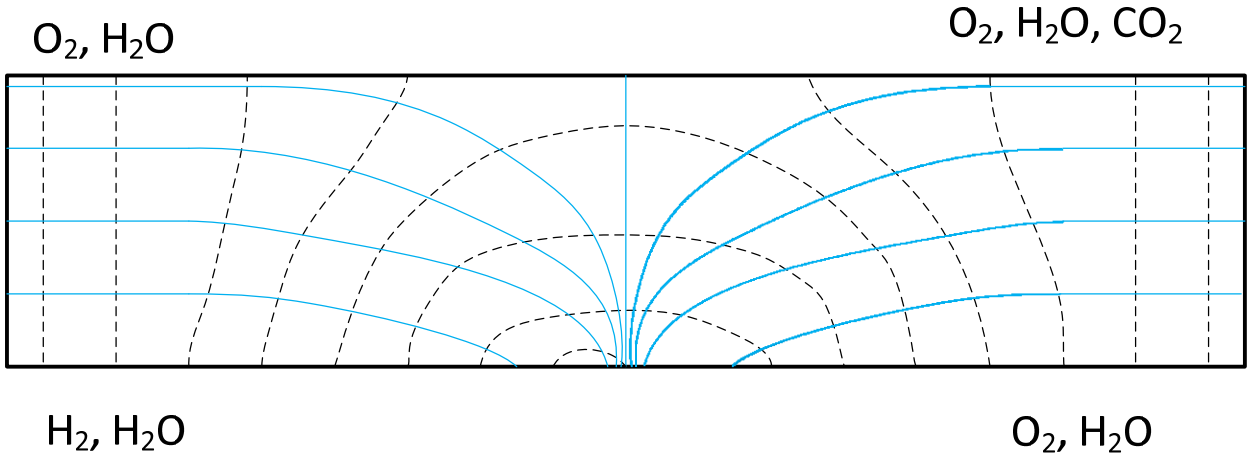
and

$i_o^2 = 10^{-10}$ A m^{-2},

we can generate the plot and observe that under these conditions the solution potential is quite negative.



For the situation described in Problem 9.11, sketch current and potential in the separator of the fuel cell during start-stop phenomena, i.e., during the situation illustrated in the figure under Problem 9.11.



On the left side the current flow from negative to positive electrode, normal fuel cell operation.

On the right side, there is a reverse current (positive to negative). Carbon corrosion on top, the protons flow to the bottom where they react with oxygen.

The current also flows in the plan of the separator. For a thin membrane, this distance is much larger than across the membrane. There is a large potential drop in solution potential from left to right.

How does the maximum power density improve if the separator is decreased in thickness from 50 to 25 μm. Assume that there are no mass-transfer limitations.

for an ohmically limited cell

$$\text{Pmax} = \frac{U^2}{4R_\Omega} = 0.73$$

The resistance of the separator is

$$R_\Omega = \frac{L}{\kappa}$$

if L is the only thing that changes

$$\frac{P_{max,2}}{P_{max,1}} = \frac{L_1}{L_2}$$

$$P_{max,2} = P_{max,1}\frac{L_1}{L_2} = P_{max,1}\frac{50}{25}$$

Thus, the maximum power is doubled.

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PROBLEM 9-14

$V_{ref} = 0.9$ [V]

$ma = 60$ [A/g] *mass actvity, on O2 at 0.9V*

$ml = 5$ [g/m^2] *catalyst loading*

$I_{O2} = ma \cdot ml$

$I_{ref} = 1$ [A/m2]

$Tk = 353.15$ [K]

$Rg = 8.314$ [J/mol-K]

$F = 96485$ [Coulomb/mol]

$$TS = 2.303 \cdot Rg \cdot \frac{Tk}{F}$$

calculate constant from I_{O2}

$$Const = V_{ref} + TS \cdot \mathbf{log}\left[\frac{I_{O2}}{I_{ref}}\right]$$

adjust for partial pressure of oxygen

$p_{ref} = 100$ [kPa]

$p_{o2} = 21$ [kPa]

$$V_c = Const + TS \cdot \left[\mathbf{log}\left(\frac{p_{o2}}{p_{ref}}\right) - \mathbf{log}\left(\frac{I}{I_{ref}}\right) + \mathbf{log}\left(1 - \frac{I_{load}}{j_d}\right)\right] - R \cdot I$$

$j_d = 15000$ [Coulomb/m^2-s]

$R = 0.00001$ [V-s-m^2/Coulomb]

$I_c = 10$ [Coulomb/m^2-s] *crossover current*

$I = I_{load} + I_c$

$pow = V_c \cdot I_{load}$

I=1000

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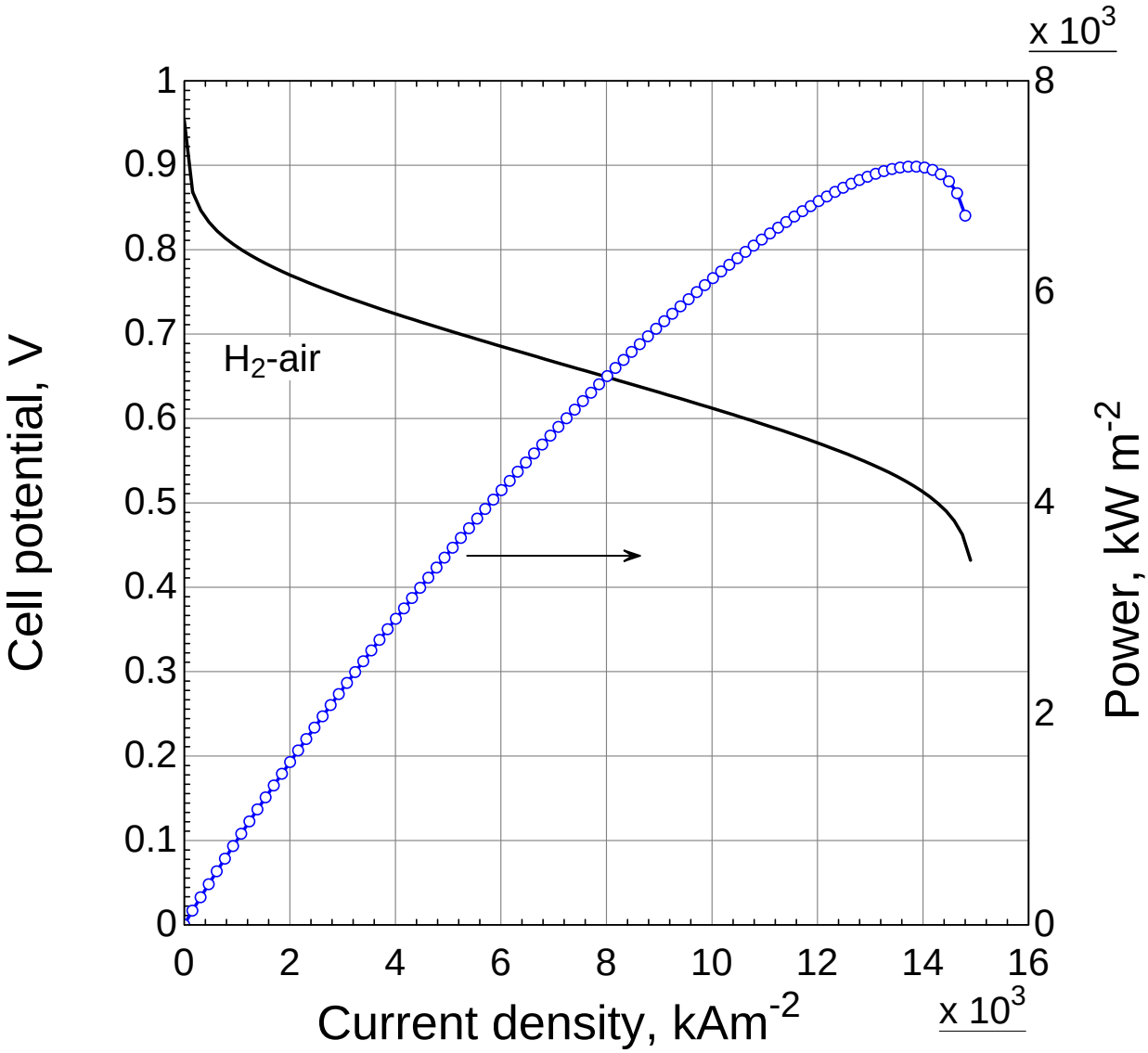


You are evaluating a new technology for a hydrogen-air fuel cell. The incumbent is the traditional proton-exchange membrane fuel cell (PEMFC). For both fuel cells, the overall reaction is

$$H_2 + 0.5\,O_2 \rightarrow H_2O.$$

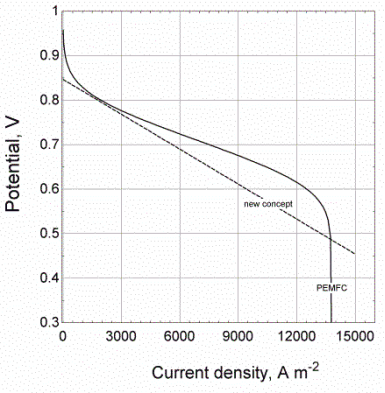
At the anode of the PEMFC, hydrogen is oxidized; and at the cathode, oxygen is reduced. It is well known that for PEMFCs the oxygen electrode is the major limitation. Although the anode reaction is unchanged, the new approach breaks the oxygen reduction reaction into two easier parts. A mediator is an electroactive species that acts as an electron shuttle. At the positive electrode, the mediator (M) reacts as follows

$$M_{ox}. + e^- \rightarrow M_{red}.$$

In a separate nonelectrochemical reaction, the mediator is regenerated outside the cell.

$$O_2 + 4H^+ + 4M_{red} \rightarrow 2H_2O + 4M_{ox}.$$

On the right are two polarization curves, one for the PEMFC and one for the new concept. Both curves are taken at 80 °C.



Compare and contrast the polarization curves of the two types of fuel cells. Specifically address, the open-circuit potential, as well as kinetic, ohmic, and mass-transfer losses.

The PEMFC polarization data are typical: the open-circuit potential is well below the thermodynamic value (U^{θ}=1.229 V) due to the irreversibility of the oxygen reduction reaction and a small amount of hydrogen permeation through the membrane, at low current densities there is a sharp decrease in potential with current (Tafel region), this is followed by a linear region, and lastly a mass-transfer limited region.

In contrast, the polarization curve for the mediator reaction is quite different. For this new concept the polarization curve is linear across a large range of current densities. This behavior suggests that the reaction is facile, and for all intents and purposes the cell is ohmically limited.

Just considering the IV relationship, the PEMFC would have a better efficiency (higher potential) over nearly all of the current densities. Though not immediately obvious, the new concept would have a slightly higher peak power.

Advantages: likely that the new concept does not require platinum or another precious metal catalyst

Disadvantage: another operation/device (regenerator) is required as well as a recirculating pump.

In Illustration 9.5, it was assumed that the hydrogen crossover current was 10 $A \cdot m^{-2}$. Estimate the permeability (Equation 4.72) for hydrogen through the membrane. Assume c is 30,000 mol m^{-3}. There is also permeation of oxygen across the membrane. The oxygen permeation is smaller than hydrogen, but not insignificant. Justify why this crossover is ignored in calculating the open-circuit potential in Illustration 9.5.

From Equation 4.71

$$J_i = \left[\frac{D_i}{H_i}\right]\frac{p_i c}{\delta}$$

the reaction of hydrogen is

$$\mathrm{H_2} \rightarrow 2\mathrm{H^+} + 2\mathrm{e^-}$$

the current associated with crossover of hydrogen is therefore

$$i_{\mathrm{xo}} = nFJ_{\mathrm{H_2}} = 2F\left[\frac{D_{\mathrm{H_2}}}{H_{\mathrm{H_2}}}\right]\frac{p_{\mathrm{H_2}} c}{\delta}$$

the quantity in brackets is the permeability

$$\left[\frac{D_{\mathrm{H_2}}}{H_{\mathrm{H_2}}}\right] = P_{\mathrm{H_2}} = \frac{i_{\mathrm{xo}}}{2F}\frac{\delta}{p_{\mathrm{H_2}} c} = 8.6 \times 10^{-19}$$

Both oxygen and hydrogen crossover represent chemical shorts: oxygen crossover polarizes the anode, whereas hydrogen crossover polarizes the cathode. Because the hydrogen reaction is fast compared to the oxygen reduction reaction, the effect of hydrogen crossover is much larger on the potential of the cell.

You are investigating mass-transfer limitations in a new cathode structure that your research group has developed for a PEM fuel cell. Consider an electrode with possible limitations to mass transfer in either the gas or liquid phase as illustrated in the cartoon on the right.

a. Using the figure as a guide, develop a relationship for an overall mass-transfer coefficient in terms of a pressure driving force; in other words, determine the expression for K in the equation

$$N_{O_2} = K\left(p^1_{O_2} - p^*_{O_2}\right)$$

where the concentration at L is expressed in terms of p_i*, the hypothetical partial pressure in equilibrium with the solution at composition x_i; that is, $p_i^* = Hx_i$. The final answer should include the following parameters

k_c, mass-transfer coefficient for gas phase m·s^{-1}
L, the thickness of the liquid film, m
c_T, the total concentration in the liquid, mol m^{-3}
D, diffusion coefficient of oxygen in the liquid, m^2 s^{-1}
H, Henry's law coefficient

b. Data have been collected for the limiting current on air (21% oxygen with balance nitrogen) and Helox (21% oxygen with the balance helium). The limiting currents and the binary gas-phase diffusivity coefficients are given below. These were collected at ambient pressure and 80 °C.

	Limiting current, [A m^{-2}]	Diffusivity of oxygen, $\mathcal{D}_{O_2,y}$
Air	15,000	2.47x10^{-5} m^2 s^{-1}
Helox	19,500	8.97x10^{-5} m^2 s^{-1}

Assume that the Sherwood number is a constant, 3.66. The following additional data are provided

D_{O2}, diffusion coefficient for liquid phase	H_{O2}/c_T, Henry's law constant
3.0 x10^{-9} m^2 s^{-1}	8.0 x10^4 Pa m^3 mol^{-1}

Estimate the fraction of mass-transfer resistance that can be ascribed to the gas phase. What does this suggest about the thickness of the liquid film?

In the liquid

$$N_{O_2} = D_{O_2}\frac{\left(c^i_{O_2} - c^L_{O_2}\right)}{L}$$

and for the gas

$$N_{O_2} = \frac{k_c}{RT}\left(p^\infty_{O_2} - p^i_{O_2}\right)$$

use $p_{O_2} = Hx_{O_2}$ to eliminate the concentration from the liquid expression

$$N_{O_2} = \frac{D_{O_2}}{L}\frac{c}{H_{O_2}}\left(p^i_{O_2} - p^*_{O_2}\right)$$

The two expressions for oxygen flux can be written as

$$N_{O_2}\frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T} = p^i_{O_2} - p^*_{O_2}$$

$$N_{O_2}\frac{RT}{k_c} = p^\infty_{O_2} - p^i_{O_2}$$

These are added together to eliminate the interfacial value

$$N_{O_2}\left\{\frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T} + \frac{RT}{k_c}\right\} = p^\infty_{O_2} - p^*_{O_2}$$

or we can define an overall mass-transfer coefficient

$$N_{O_2} = K\left(p^\infty_{O_2} - p^*_{O_2}\right)$$

where

$$K^{-1} = \frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T} + \frac{RT}{k_c}$$

b) $$i = nFN_{O_2}$$

n=4, and the limiting current corresponds to $p^*_{O_2} = 0$

$$N_{O_2} = \left(\frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T} + \frac{RT}{k_c}\right)^{-1} p^\infty_{O_2}$$

Using the definition of the Sherwood number, which is taken as a constant in this problem

$$k_c = \frac{3.66\mathcal{D}_{O_2,y}}{L_c}$$

$$i_{lim} = nF\left(\frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T} + \frac{RTL_c}{3.66\mathcal{D}_{O_2,y}}\right)^{-1} p^\infty_{O_2}$$

Using the data, solve L=16 nm, and L_c=3.8 mm

For air

$$\frac{1}{K} = \frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T} + \frac{RT}{k_c}$$

$$\text{total} = \text{film} + \text{gas phase}$$

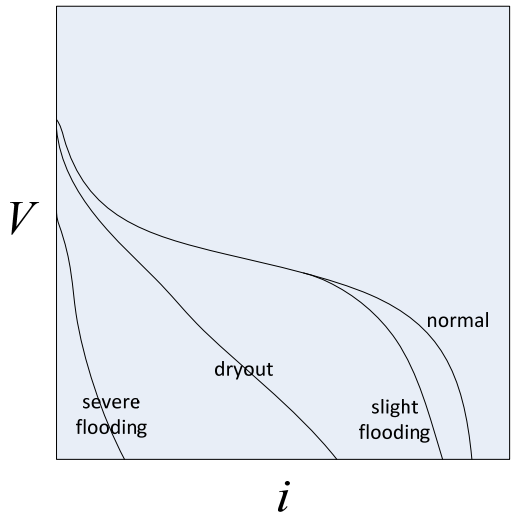
fraction in the liquid is

$$\frac{\frac{L}{D_{O_2}}\frac{H_{O_2}}{c_T}}{1/K} = 0.72$$

How would flooding affect the polarization curve of a PEM fuel cell. What about dryout? Sketch the polarization curves for normal, dryout, slight flooding, and severe flooding operation.

The main effect of dryout is to increase the resistance of the membrane separator.

Flooding would have two effects. moderate levels of flooding would reduce the limiting current, severe flooding would greatly restrict access of the oxygen to the catalysts resulting in a large polarization at all current densities.

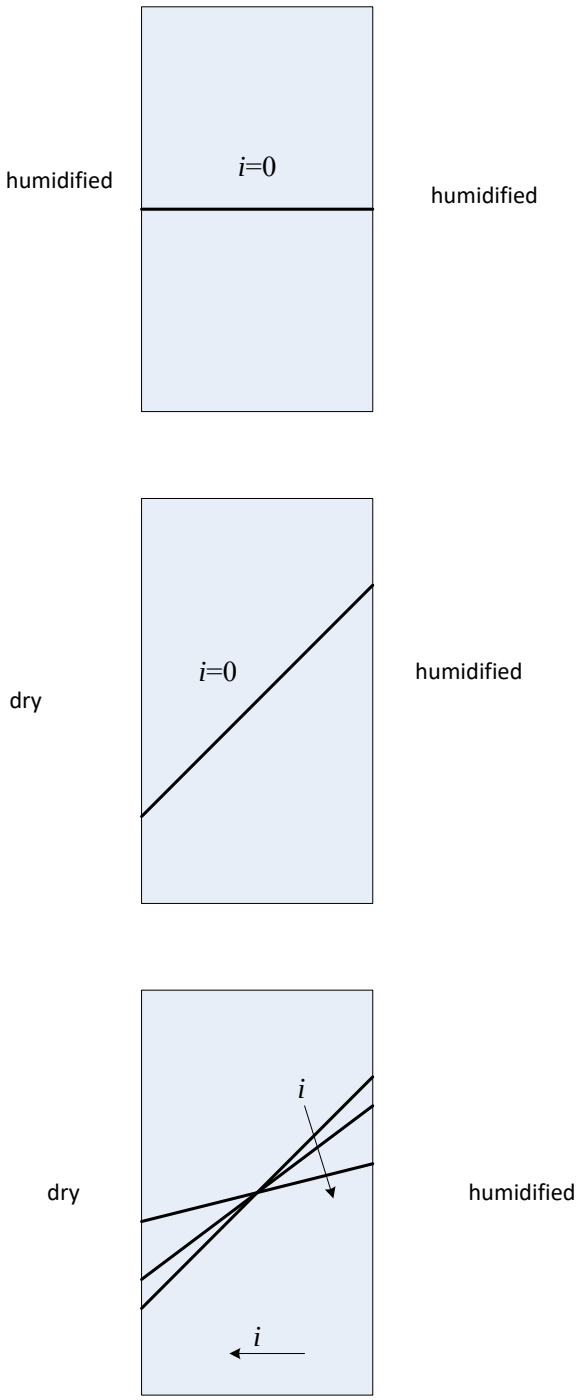


Sketch composition of water across membrane in a PEM fuel cell for the following conditions

Both streams humidified, no current flow

One humidified, one dry , no current

One humidified, one dry , low and high current (from humidified to dry)



Data for the polarization of a solid oxide fuel cell/electrolyzer are provided below. *J. Electrochem. Soc.*, **158**, B514-B525 (2011). These potentials are reported with respect to a hydrogen reference electrode. The temperature of operation is 973 K. The ohmic resistance of the cell is 0.067 Ω-cm^2. After removing ohmic polarization, how well can the data be represented by Butler-Volmer kinetic expression? Discuss whether the BV expression is appropriate for these data?\

i, [A·m^{-2}]	V_{cell}, [V]	i, [A·m^{-2}]	V_{cell}, [V]
-6981	1.5006	930	0.9047
-4871	1.3554	2799	0.7545
-4871	1.3554	4753	0.6020
-2946	1.2074	6836	0.4518
-967	1.0549	9328	0.3000

Using the ohmic resistance provided, the data are corrected for IR, polarization of the anode is neglected.

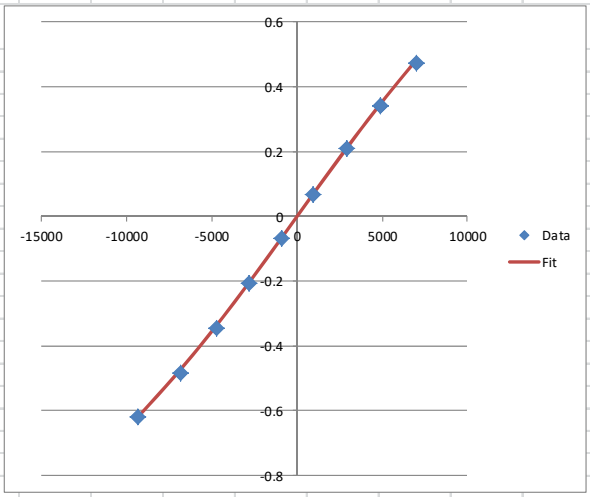
$$V_{cell} = V_{OCV} - iR_{\Omega} - \eta_{cath}$$

or

$$\eta_{cath} = V_{OCV} - V_{cell,corr}$$

The corrected data are fit to the Butler Volmer equation as was described in Chapter 3.

		F/RT	11.92716		
	0.59	c	0.106999		
	0.42	i	5336.409		
	0.41	a	0.508697		
	U=0.98				
iR free	overpotential	Current density	calculated current		error
1.453849	0.473849	6980.82	6854.746		-126.074274
1.322727	0.342727	4870.62	4818.432		-52.1881704
1.322727	0.342727	4870.62	4818.432		-52.1881704
1.187634	0.207634	2945.71	2861.317		-84.3930802
1.04839	0.06839	967.119	932.7028		-34.4161899
0.910956	-0.06904	-930.026	-941.638		-11.6124641
0.773292	-0.20671	-2798.88	-2848.26		-49.3774323
0.633852	-0.34615	-4753.22	-4869.61		-116.39143
0.497573	-0.48243	-6836.36	-6994.03		-157.673831
0.362492	-0.61751	-9328.21	-9308.87		19.33507643
					71003.42638



The fit is reasonable, but the reaction at the cathode is

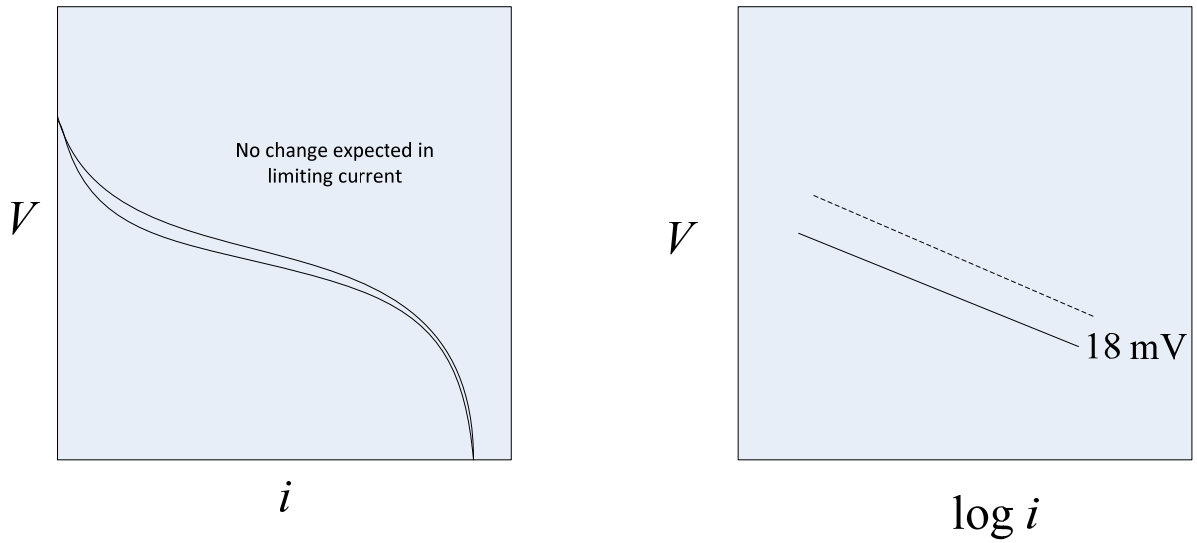
$$O_2 + 4e^- \rightarrow 2O^{2-}$$

n=4, we expect that $n = \alpha_a + \alpha_c$. This is clearly not true here. Although the fit is ok, the Butler Volmer mechanism is not correct. In fact, we could come up with several good fits to the data, they are not unique.

If the loading of the cathode of a PEM fuel cell is doubled, what would you expect to happen to polarization curve? What if the pressure is doubled?

Think about the specific activity of the catalyst being fixed (0.9 V, oxygen, B[A g^{-1}]. If the loading is doubled then the current density at 0.9 V is also doubled. In effect the polarization curve is shifted up by

$$2.303\frac{RT}{F}\log 2 = 18\ \text{mV}$$



Change in pressure. Oxygen reduction reaction is first order in the partial pressure of oxygen and governed by Tafel kinetics. Change in kinetic region will be the same as for doubling loading. However, a change in pressure will increase the limiting current.

Derive Equation 9.24 for the concentration overpotential of the anode of a solid oxide fuel cell assuming that only the thermodynamic contribution is important (see Chapter 4).

$$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$$

Because of transport limitations, the partial pressure of hydrogen is lower at the electrode surface and the partial pressure of water is larger compared to the bulk value.

Use thermodynamics (Nernst equation)

$$U_a = U_a^\theta - \frac{RT}{nF} \ln \left[\prod \left({}^{p_i}/_{p^o} \right)^{s_i} \right]$$

$$\eta_{c,a} = U_a(bulk) - U_a(surface)$$

$$\eta_{c,a} = -\frac{RT}{2F} \ln \left(\frac{p_{H_2O,b}}{p_{H_2O,s}} \frac{p_{H_2,s}}{p_{H_2,b}} \right)$$

Estimate of the concentration polarization at the anode.

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problem 9-23

limiting current of cathode in SOFC

$R = 8.314$ [J/mol-K]

$T = 1173$ [K]

$p = 100$ [kPa]

$F = 96485$ [Coulomb/mol]

$n = 4$

$L = 0.0007$ [m] *thickness of anode support*

$\varepsilon = 0.5$ *porosity of anode support*

$\tau = 6$ *tortuosity of anode support*

Estimate diffusivity of oxygen in nitrogen from kinetic theory

any water vapor is neglected

G1$ = 'nitrogen'

G2$ = 'oxygen'

$D = \mathbf{D}_{12,gas}(G1\$, G2\$, T, p)$

$$Deff = D \cdot \frac{\varepsilon}{\tau}$$

$po_o = 0.21 \cdot p$ *partial pressure of oxygen outside support*

$pn_o = p - po_o$ *partial pressure of nitrogen in bulk, outside support*

Use Fick's law to determine partial pressures in anode interlayer

$cf = 0.001$ [kPa/Pa]

$$po = po_o - cf \cdot I \cdot R \cdot T \cdot \frac{L}{n \cdot F \cdot Deff}$$ *partial pressure of oxygen in cathode interlayer*

$pn = p - po$ *partial pressure of nitrogen in cathode interlayer*

$po = 0$ [kPa] *correspons to a limiting current density*

SOLUTION

Unit Settings: SI K kPa kJ mass deg

cf = 0.001 [kPa/Pa]
Deff = 0.00001776 [m^2/s]
F = 96485 [Coulomb/mol]
D = 0.0002131 [m^2/s]
ε = 0.5
G1$ = 'nitrogen'

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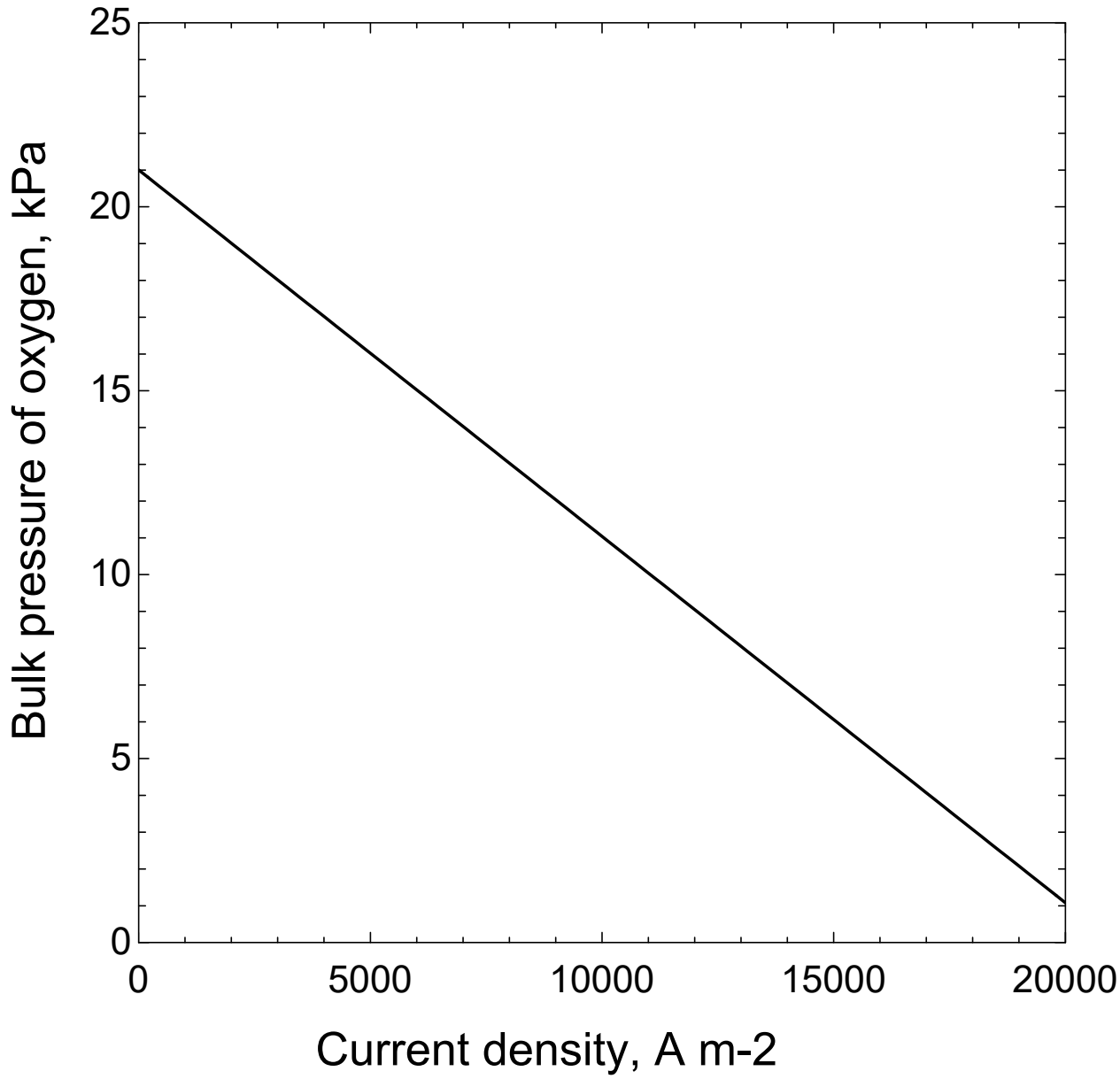
G2$ = 'oxygen'
L = 0.0007 [m]
p = 100 [kPa]
p_{n_o} = 79 [kPa]
p_{o_o} = 21 [kPa]
T = 1173 [K]

I = 21083 [Coulomb/m^2-s]
n = 4
pn = 100 [kPa]
po = 0 [kPa]
R = 8.314 [J/mol-K]
τ = 6

No unit problems were detected.



From the data provided, calculate the transference number of oxygen for doped ceria and YSZ. How would open-circuit potentials of the two cells compare?

YSZ	κ=7 S m^{-1}	σ=0.1 S m^{-1}
doped ceria	κ=15 S m^{-1}	σ=10 S m^{-1}

Use Equation 9-21

$$t_{O^{2-}} = \frac{\kappa}{\kappa + \sigma}$$

For YSZ

$$t_{O^{2-}} = \frac{7}{7 + 0.1} = 0.99$$

For Ceria

$$t_{O^{2-}} = \frac{15}{15 + 10} = 0.6$$

Because the transference number is much lower for ceria cells made with this material will have a lower open circuit potential. Effectively, the high electronic conductivity amounts to a short in the cell.

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Problem 9-25

T = 1073 [K]

R = 8.314 [J/mol-K]

F = 96485 [coulomb/mol]

i=1000 [coulomb/m^2-s]

yh = 0.9 *mole fraction of hydrogen in bulk*

yo = 0.21 *mole fraction of oxygen in bulk*

p = 100000 [Pa]

Do = 0.00019 [m^2/s]

Dh = 0.00078 [m^2/s]

ea = 0.45

ta = 2.5

ec = 0.4

tc = 3

L_a = 0.00075 [m] *electrolyte supported*

L_c = 0.00005 [m]

σ = 10 [1/Ω-m]

Calculation of open-circuit potential

from Figure 9.4, at 800 C

Uo = 0.9794 [V]

adjust for concentration of reactants

$$U = Uo + R \cdot \frac{T}{2 \cdot F} \cdot \ln\left[ph \cdot \frac{\left[\frac{po}{p}\right]^{0.5}}{pw} \right]$$

Ohmic polarization, only consider electrolyte

L = 0.00004 [m] *electrolyte thickness*

$$\eta_{ohm} = i \cdot \frac{L}{\sigma}$$

Kinetic polarization

cathode

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$ic = 4000$ [coulomb/m^2-s]

$Cc = 0.2$ [V]

$$\eta_c = Cc \cdot \mathbf{arcsinh}\left[\frac{i}{ic}\right]$$

anode, use linear kinetics

$ioa = 5300$ [coulomb/m^2-s]

$$i = ioa \cdot 2 \cdot \frac{F}{R \cdot T} \cdot \eta_a$$

mass transfer correction

$$ph = p \cdot yh - \frac{i \cdot R \cdot T \cdot L_a}{2 \cdot F \cdot Dh \cdot \frac{ea}{ta}}$$ *equimolar counter diffusion*

$pw = p - ph$

*po=p*yo*

$$i = 4 \cdot F \cdot \frac{p}{R \cdot T} \cdot Do \cdot \frac{ec}{L_c \cdot tc} \cdot \mathbf{ln}\left[\frac{po - p}{yo \cdot p - p}\right]$$

Potential of Cell and power

$$V_{cell} = U - \eta_{ohm} - |\eta_c| - |\eta_a|$$

$Pow = V_{cell} \cdot i$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

(Table 1, Run 100)

$Cc = 0.2$ [V]
$Dh = 0.00078$ [m^2/s]
$Do = 0.00019$ [m^2/s]
$ea = 0.45$
$ec = 0.4$
$\eta_a = 0.2966$ [V]
$\eta_c = 0.5673$ [V]
$\eta_{ohm} = 0.136$ [V]
$F = 96485$ [coulomb/mol]
$i = 34000$ [coulomb/m^2-s]
$ic = 4000$ [coulomb/m^2-s]
$ioa = 5300$ [coulomb/m^2-s]
$L = 0.00004$ [m]
$L_a = 0.00075$ [m]
$L_c = 0.00005$ [m]

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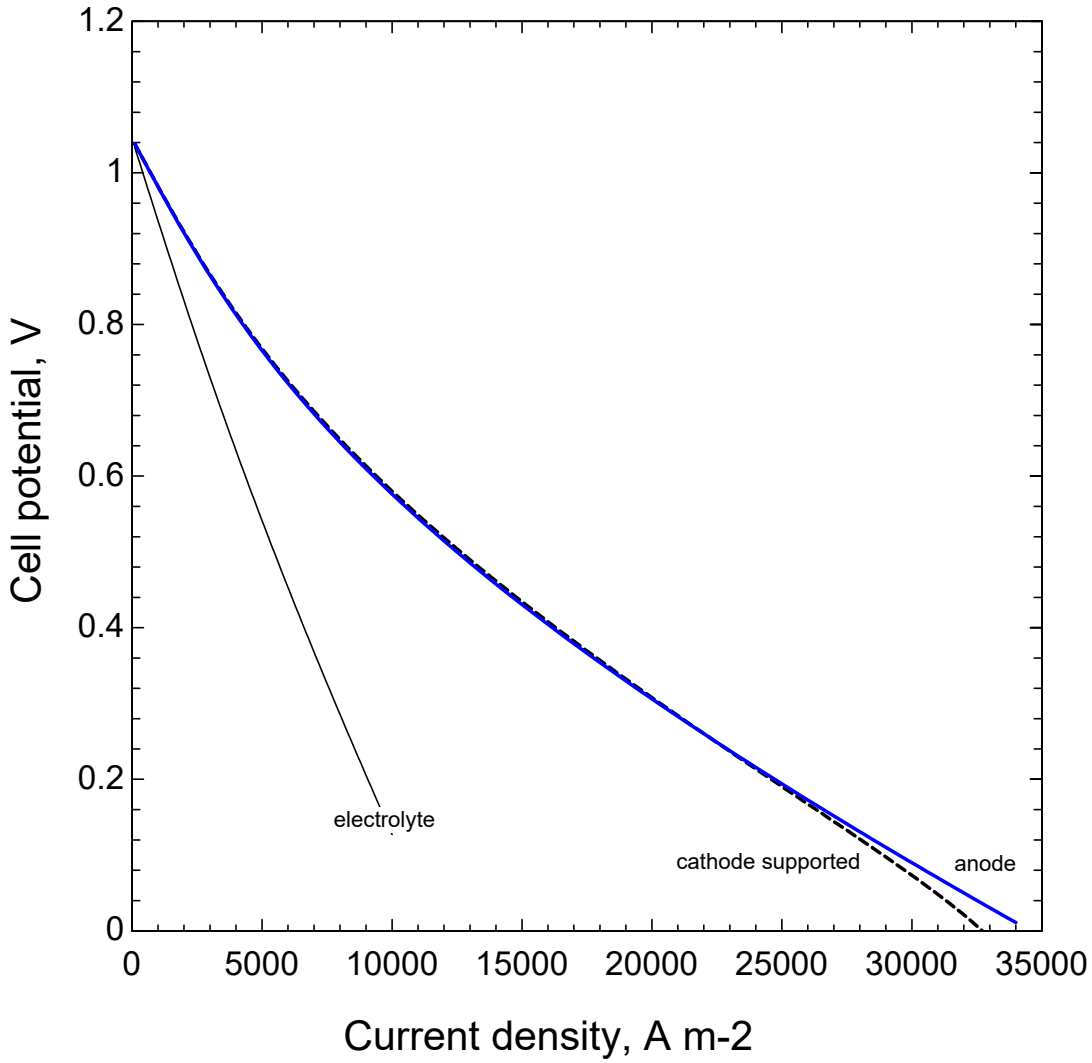
p = 100000 [Pa]
ph = 81604 [Pa]
po = 19765 [Pa]
Pow = 370.5 [W/m^2]
pw = 18396 [Pa]
R = 8.314 [J/mol-K]
σ = 10 [1/Ω-m]
T = 1073 [K]
ta = 2.5
tc = 3
U = 1.011 [V]
Uo = 0.9794 [V]
V_{cell} = 0.0109 [V]
yh = 0.9
yo = 0.21

No unit problems were detected.



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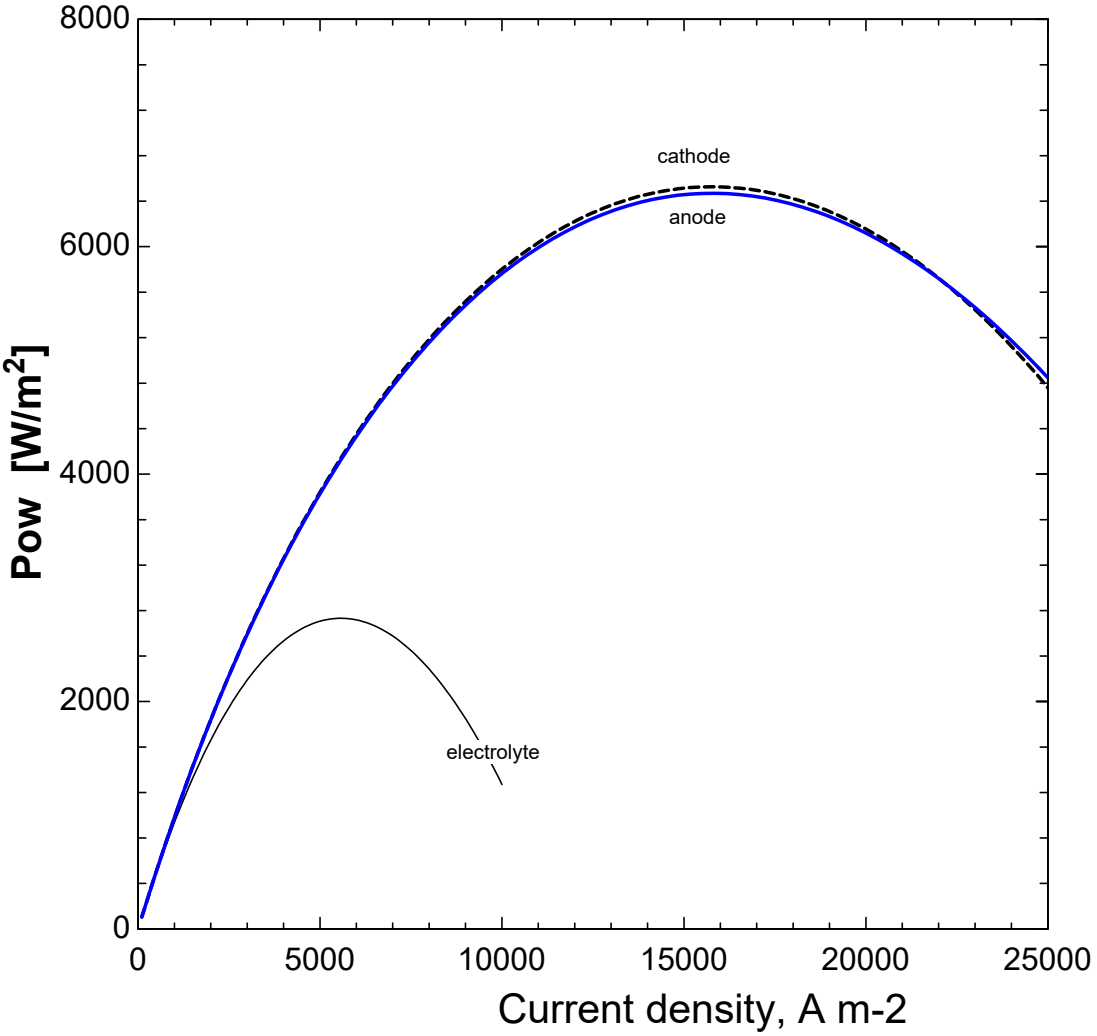

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Problem 9-26

$R = 8.314$ [J/mol-K]

$T = 923$ [K]

$F = 96485$ [coulomb/mol]

at 650 C

$Uo = 1.05$ [V]

$pr = 100000$ [Pa] *reference pressure and total pressure*

$pa = 20000$ [Pa]

$pc = 10000$ [Pa]

$pr = pc + po \cdot 4.76$ *calculate pressure of O2, assuming air*

$pr = pa + ph + pw$

$6 \cdot ph = 19 \cdot pw$ *not enough information provided, assume hydrogen and water ratio the same as in problem 9.6*

use Nerst equation to adjust potential

$$U = Uo + R \cdot \frac{T}{2 \cdot F} \cdot \ln\left[\frac{ph}{pr} \cdot \sqrt{\frac{po}{pr}} \cdot \frac{pc}{pa} \cdot \frac{pw}{pr}\right]$$

ohmic losses only in cell

$$V_{cell} = U - i \cdot \frac{L}{\kappa}$$

$\kappa = 100$ [1/Ω-m]

$L = 0.0005$ [m]

$i = 2000$ [A/m^2]

$Pow = i \cdot V_{cell}$

(c) with the information given, the cell resistance is already quite low, and no information on transport polarization is provided

a three fold increase in power, therefore, requires roughly a three-fold increase in current density as the same potential, corresponding to a thickness of 1/3 the original

actual calculation

$$3 \cdot Pow = i_n \cdot \left[U - i_n \cdot \frac{L_n}{\kappa}\right]$$

$$V_{cell} = U - i_n \cdot \frac{L_n}{\kappa}$$

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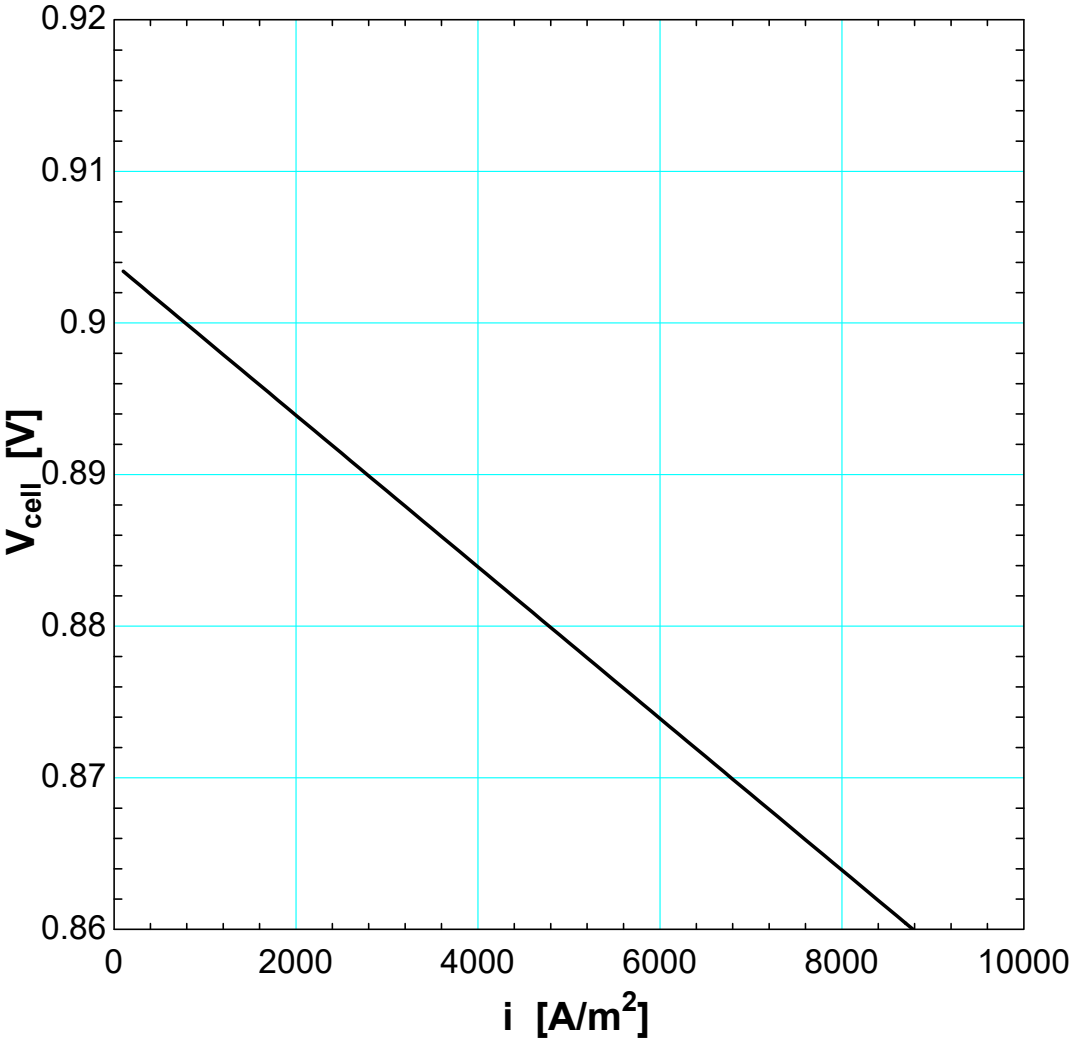
SOLUTION

Unit Settings: SI C kPa kJ mass deg

F = 96485 [coulomb/mol]
i_n = 6000 [A/m^2]
L = 0.0005 [m]
pa = 20000 [Pa]
ph = 60800 [Pa]
Pow = 1788 [W/m^2]
pw = 19200 [Pa]
T = 923 [K]
Uo = 1.05 [V]

i = 2000 [A/m^2]
κ = 100 [1/Ω-m]
L_n = 0.0001667 [m]
pc = 10000 [Pa]
po = 18908 [Pa]
pr = 100000 [Pa]
R = 8.314 [J/mol-K]
U = 0.9039 [V]
V_{cell} = 0.8939 [V]

No unit problems were detected.



Using the definition of efficiency given by Equation 10-3, what is the maximum thermal efficiency of a hydrogen/oxygen fuel cell at 25 °C, standard conditions?

$$\eta_{th} = \frac{\text{net electrical output}}{\text{enthalpy of combustion}}$$

this is maximized when

$$\eta_{th} = \frac{\Delta G}{\Delta H}$$

For the reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(\ell)}$$

Using data from Appendix C.

$$\Delta G^o_{f,H_2O} = -237.129 \text{ kJ mol}^{-1}$$
$$\Delta H^o_{f,H_2O} = -285.83 \text{ kJ mol}^{-1}$$

$$\eta_{th} = \frac{\Delta G}{\Delta H} = \frac{237.129}{285.83} = 0.83$$

If the product, water, is a gas

$$\eta_{th} = \frac{\Delta G}{\Delta H} = \frac{228.572}{241.572} = 0.95$$

A fuel cell operating on methane produces 100 kW of gross electrical power. Calculate the voltage and thermal efficiency given all of the following

1) The individual cells are operating at a potential of 0.65 V and gaseous water is produced at standard conditions

2) 75 % of the fuel is converted to electricity (the balance is combusted external to the fuel cell to drive the reformation process)

3) 5 % of the electrical output is consumed by ancillary equipment and losses in power conversion

Using Equation 9.2

$$\eta_V = \frac{V}{U} = \frac{VnF}{-\Delta G}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)}$$

n=8,

$$\Delta G^o_{Rx} = 2\Delta G^o_{f,H_2O} + \Delta G^o_{f,CO_2} - \Delta G^o_{f,CH_4}$$

$$\Delta G^o_{Rx} = 2(-228.572) + (-394.359) - (-50.5) = 801 \text{ kJ mol}^{-1}$$

$$\eta_V = \frac{0.65(8)(96485)}{801{,}000} = 0.63$$

b) use Equation 10.4

$$\eta_{th} = \eta_f \times \eta_{V,t} \times \eta_{pc} \times \eta_{mech}$$

$$\eta_{V,t} = \eta_V \left(\frac{\Delta G}{\Delta H}\right)$$

$$\Delta H^o_{Rx} = 2(-241.572) + (-393.509) - (-74.6) = 802.5 \text{ kJ mol}^{-1}$$

$$\eta_{V,t} = \eta_V \left(\frac{\Delta G}{\Delta H}\right) = 0.63\left(\frac{801}{802.5}\right) = 0.63$$

$$\eta_{pc} \times \eta_{mech} = \frac{net\ power}{gross\ power} = \frac{(1-0.05)100}{100} = 0.95$$

$$\eta_{th} = \eta_f \times \eta_{V,t} \times \eta_{pc} \times \eta_{mech} = (0.75)(0.63)(0.95) = 0.45$$

How would the results of Problem 10-2 change if we assume that the water is produced as a liquid?

Using Equation 9.2

$$\eta_V = \frac{V}{U} = \frac{VnF}{-\Delta G}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(\ell)}$$

n=8,

$$\Delta G^o_{Rx} = 2\Delta G^o_{f,H_2O} + \Delta G^o_{f,CO_2} - \Delta G^o_{f,CH_4}$$

$$\Delta G^o_{Rx} = 2(-237.129) + (-394.359) - (-50.5) = 818.12 \text{ kJ mol}^{-1}$$
$$\Delta H^o_{Rx} = 2(-285.83) + (-393.509) - (-74.6) = 890.57 \text{ kJ mol}^{-1}$$

$$\eta_V = \frac{0.65(8)(96485)}{818{,}120} = 0.61$$

b) use Equation 10.4

$$\eta_{th} = \eta_f \times \eta_{V,t} \times \eta_{pc} \times \eta_{mech}$$

$$\eta_{V,t} = \eta_V \left(\frac{\Delta G}{\Delta H}\right)$$

$$\eta_{V,t} = \eta_V \left(\frac{\Delta G}{\Delta H}\right) = 0.61 \left(\frac{818.12}{890.57}\right) = 0.56$$

$$\eta_{pc} \times \eta_{mech} = \frac{net\ power}{gross\ power} = \frac{(1 - 0.05)100}{100} = 0.95$$

$$\eta_{th} = \eta_f \times \eta_{V,t} \times \eta_{pc} \times \eta_{mech} = (0.75)(0.56)(0.95) = 0.40$$

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PROBLEM 10-04

Equilibrium potential of cell as a function of temperature

comes from Fuller's thesis

$Cp=a+bT+c/T^2$

$Uo = 1.184$ [V] *equilibrium potential at 298, assuming gaseous water*

$To = 298.15$ [K]

$F = 96485$ [coulomb/mol]

$DHo = -241572$ [J/mol] *one mole of water*

$n = 2$

Heat capacity data for gases

$da = [30.54 - 0.5 \cdot 29.96 - 27.28] \cdot 1$ [J/mol-K]

$db = \left[\frac{10.29 - 0.5 \cdot 4.184 - 3.26}{1000}\right] \cdot 1$ [J/mol-K^2]

$dc = [0 + 0.5 \cdot 1.67 - 0.5] \cdot 100000 \cdot 1$ [J-K/mol]

$$U = \frac{T}{To} \cdot Uo + \frac{T}{2 \cdot F} \cdot \left[-DHo \cdot \left(\frac{1}{T} - \frac{1}{To}\right) + da \cdot \left(\ln\left[\frac{T}{To}\right] + \frac{To}{T} - 1 \right) + \frac{(T - To)^2}{2 \cdot T} \cdot \left(db + \frac{dc}{T \cdot To \cdot To} \right) \right]$$

$G = -n \cdot F \cdot U$

$$H = DHo - da \cdot [T - To] - \frac{db}{2} \cdot [T^2 - To^2] + dc \cdot \left[\frac{1}{T} - \frac{1}{To}\right]$$

$w = \frac{G}{H}$

repeat for liquid water, below 100 C, use higher heating value

$DHlo = -285830$ [J/mol]

$Ulo = 1.229$ [V]

$dal = [30.54 - 0.5 \cdot 75.36 - 27.28] \cdot 1$ [J/mol-K]

$dbl = \left[\frac{10.29 - 3.26}{1000}\right] \cdot 1$ [J/mol-K^2]

$dcl = [0 - 0.5] \cdot 100000 \cdot 1$ [J-K/mol]

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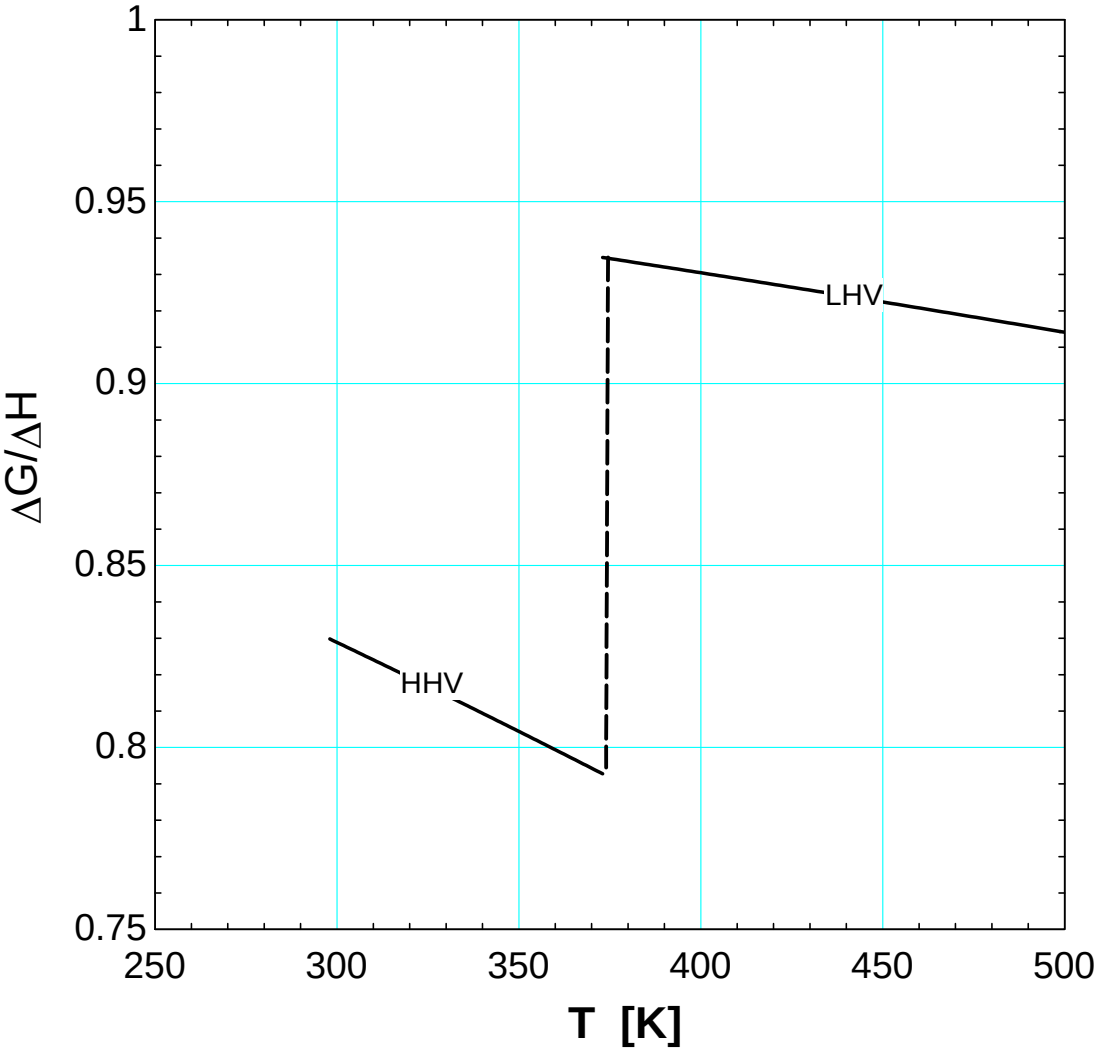
$$Ul = \frac{T}{To} \cdot Ulo + \frac{T}{2 \cdot F} \cdot \left[- DHlo \cdot \left(\frac{1}{T} - \frac{1}{To} \right) + dal \cdot \left(\ln\left[\frac{T}{To} \right] + \frac{To}{T} - 1 \right) + \frac{(T - To)^2}{2 \cdot T} \cdot \left(dbl + \frac{dcl}{T \cdot To \cdot To} \right) \right]$$

$$Gl = - n \cdot F \cdot Ul$$

$$Hl = DHlo - dal \cdot [T - To] - \frac{dbl}{2} \cdot [T^2 - To^2] + dcl \cdot \left[\frac{1}{T} - \frac{1}{To} \right]$$

$$wl = \frac{Gl}{Hl}$$



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PROBLEM 10-5

$p = 18000$ [W]

$uf = 0.98$

$t = 10800$ [s] *3 hours*

$V = 0.7$ [V]

$MW = 0.002$ [kg/mol] *molecular weight of hydrogen*

$$I = \frac{p}{V}$$ *total current*

$n = 2$

$F = 96485$ [coulomb/mol]

$$mass = MW \cdot I \cdot \frac{t}{n \cdot uf \cdot F}$$

Assume that you travel about 150 miles in 3 hours, and 35 miles/gallon

need 150/35=4.3 gallons, at about 3 kg/gallon=13 kg

SOLUTION

Unit Settings: SI C kPa J mass deg

F = 96485 [coulomb/mol]
mass = 2.937 [kg]
n = 2
t = 10800 [s]
V = 0.7 [V]

I = 25714 [A]
MW = 0.002 [kg/mol]
p = 18000 [W]
uf = 0.98

No unit problems were detected.

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PROBLEM 10-6

Part A, use equation 10-3

$$\eta_{th} = \frac{Pnet}{HC}$$

$Pnet = 35$ [W]

$\eta_{th} = 0.55$

H2+0.5O2=H2O

$x = 0$

$y = 2$

$z = 0$

$MWf = 0.002$ [kg/mol] *molecular weight of hydrogen*

$Hf_f = -0$ [J/mol]

$Hf_{CO2} = -393509$ [J/mol]

$Hf_w = -241572$ [J/mol] *assumes water vapor*

$$HC = \frac{\dot{m}}{MWf} \cdot \left[Hf_f - x \cdot Hf_{CO2} - 0.5 \cdot y \cdot Hf_w \right]$$

$t = 72 \cdot 3600 \cdot 1$ [s] *3 hours*

$mass = \dot{m} \cdot t$

part b

$F = 96485$ [coulomb/mol]

$Pg = 50$ [W]

$m_a = 0.21$ [kg] *ancillaries*

$$m_s = \frac{Pg}{sp}$$ *stack mass*

$sp = 100$ [W/kg]

$$m_{hs} = Pg \cdot \frac{t}{se}$$

$se = 1200 \cdot 3600 \cdot 1$ [J/kg]

$m_{fcs} = mass + m_a + m_s + m_{hs}$

$cf = 3600$ [J/W-h]

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$$s_{energy} = Pnet \cdot \frac{t}{m_{fcs} \cdot cf}$$

value of 655 is much higher than that of a battery (150)

Options would be 1) reduce ohmic resistance, 2) reduce power of ancillary devices, 3) improve utilization of fuel, 4) improve catalysts for oxygen reduction

SOLUTION

Unit Settings: SI C kPa J mass deg

cf = 3600 [J/W-h]
F = 96485 [coulomb/mol]
Hf_{CO2} = -393509 [J/mol]
Hf_w = -241572 [J/mol]
MWf = 0.002 [kg/mol]
$\dot{m}$ = 5.269E-07 [kg/s]
m_{hs} = 3 [kg]
Pg = 50 [W]
se = 4.320E+06 [J/kg]
s_{energy} = 655.1 [W-h/kg]
x = 0
z = 0

η^{th} = 0.55
HC = 63.64 [W]
Hf_f = 0 [J/mol]
mass = 0.1366 [kg]
m_a = 0.21 [kg]
m_{fcs} = 3.847 [kg]
m_s = 0.5 [kg]
Pnet = 35 [W]
sp = 100 [W/kg]
t = 259200 [s]
y = 2

No unit problems were detected.

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PROBLEM 10-7

$F = 96485$ [coulomb/mol]

$Voc = 1.18$ [V]

$b = 0.054$ [V]

parameters provided in problem

$j = 25500$ [A/m^2]

$jd = 30000$ [A/m^2]

$\ln[k] = -9.14$

$R = 0.000005$ [Ω-m^2]

polarization curve based on Kulokivsky paper, JES 152 (6) A1290 (2005)

$Vcell = Voc - \eta_c - R \cdot I$

$$\frac{\eta_c}{b} = \phi \cdot \ln[t] - \ln[k] - \ln\left[1 - \frac{I}{jd}\right]$$

$$t = \frac{I}{j}$$

$$\phi = 1 + \frac{t}{1 + t}$$

ancillary power

$pao = 500$ [W] *constant of 500 watts*

$pa = pao + 0.05 \cdot I \cdot Vcell \cdot A$ *proportional to current*

$Nc = 100$

$Ac = 0.04$ [m^2]

$A = Nc \cdot Ac$ *total cell area*

$Pn = I \cdot Vcell \cdot A - pa$ *net power produced*

$DHg = 241572$ [J/mol]

$$W = I \cdot \frac{A}{2 \cdot F \cdot u}$$

$u = 0.97$ *hydrogen utilization*

$$\eta = \frac{Pn}{DHg \cdot W}$$

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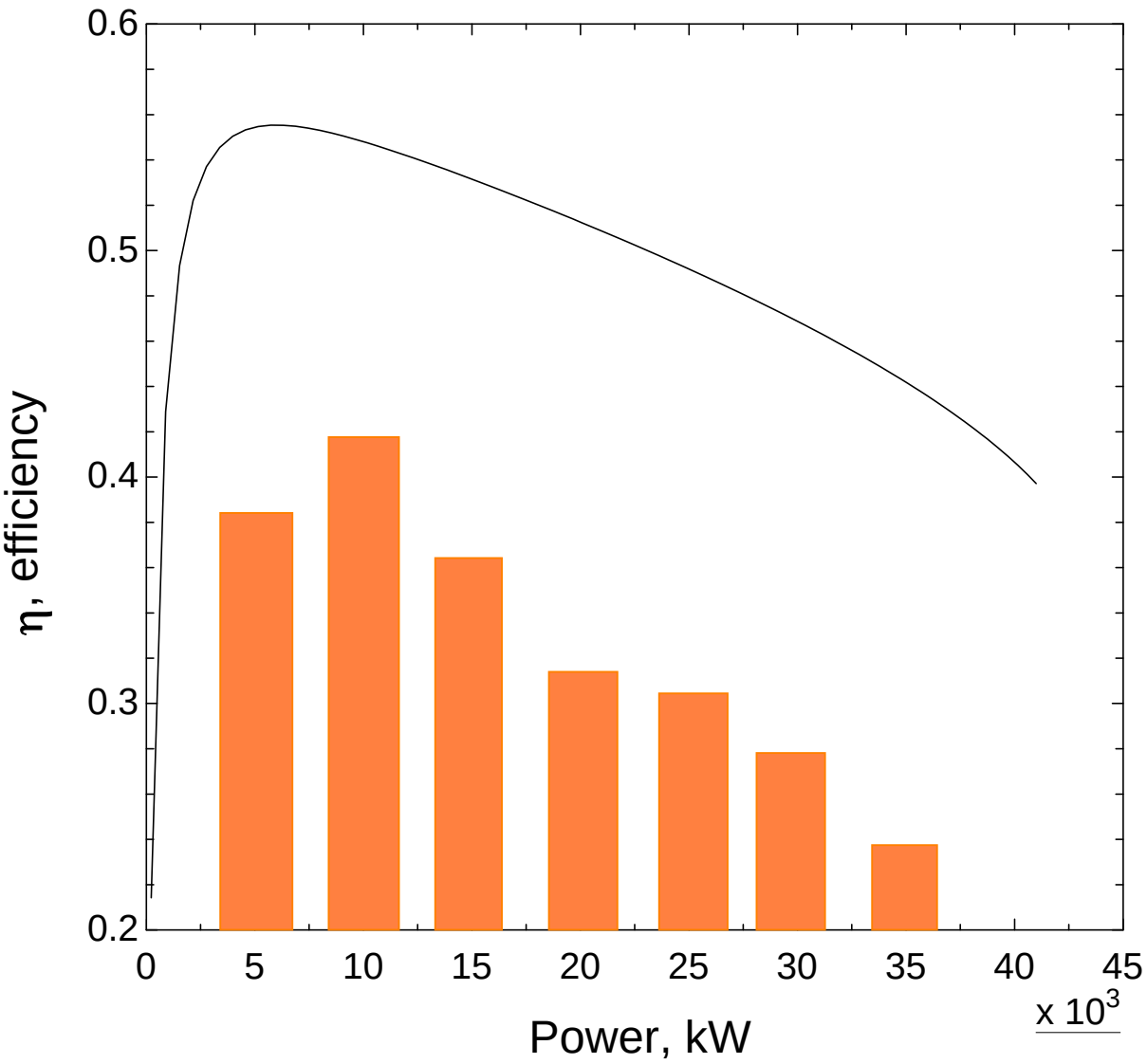
SOLUTION

Unit Settings: SI C kPa kJ mass deg

(Table 1, Run 100)

A = 4 [m^2]
Ac = 0.04 [m^2]
b = 0.054 [V]
DHg = 241572 [J/mol]
η = 0.3971
η_c = 0.534 [V]
F = 96485 [coulomb/mol]
I = 20000 [A/m^2]
j = 25500 [A/m^2]
jd = 30000 [A/m^2]
k = 0.0001073
Nc = 100
pa = 2684 [W]
pao = 500 [W]
ϕ = 1.44
Pn = 40996 [W]
R = 0.000005 [Ω-m^2]
t = 0.7843
u = 0.97
Vcell = 0.546 [V]
Voc = 1.18 [V]
W = 0.4274 [mol/s]

No unit problems were detected.



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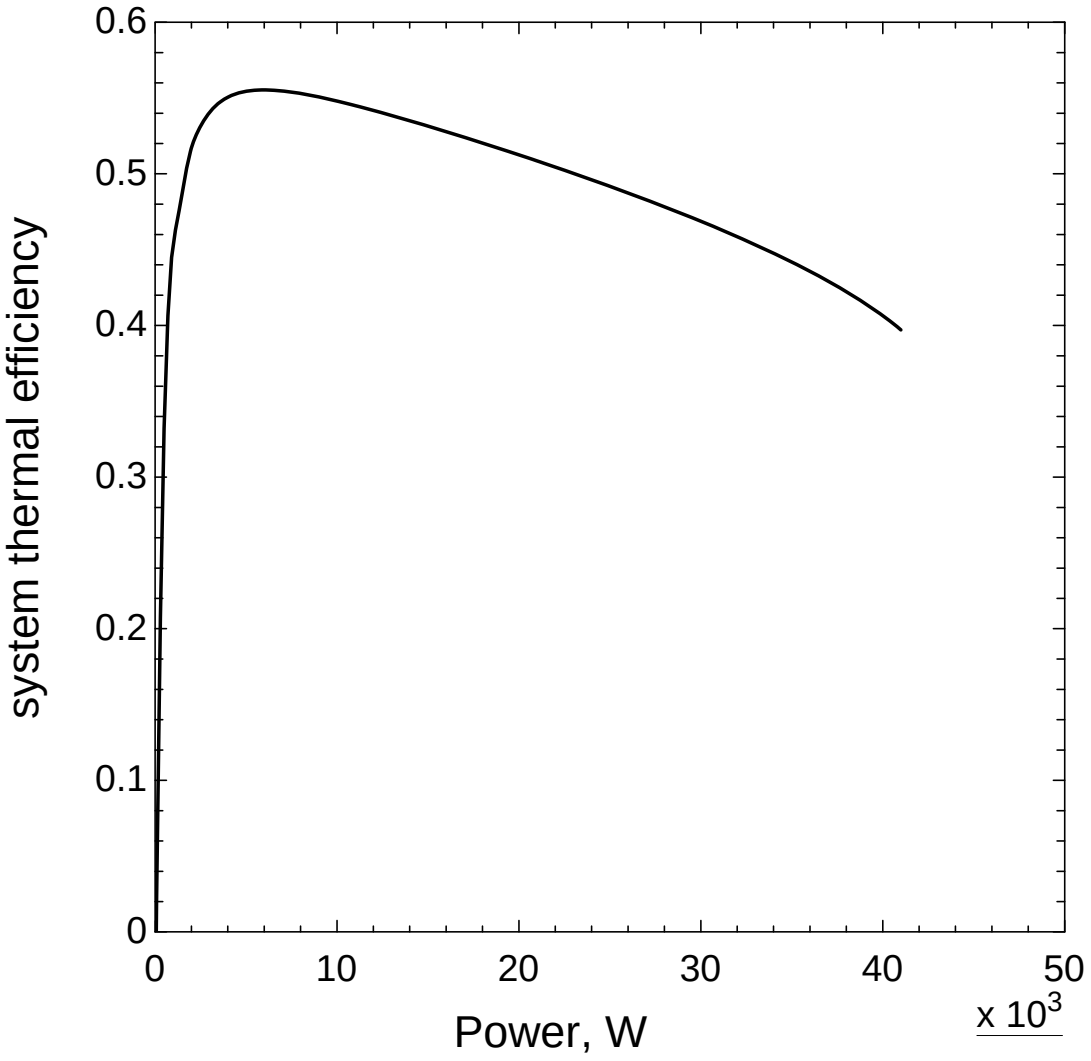

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PROBLEM 10-8

$V_{cell} = 0.4$ [V]

$i = 2000$ [A/m^2]

$P = 50$ [W]

$L_{ep} = 0.0075$ [m]

$V_s = 12$ [V]

$P = V_{cell} \cdot i \cdot A$

$N_c = \mathbf{Trunc}\left[\frac{V_s}{V_{cell}}\right]$

$A = A_c \cdot N_c$

$c_p = 0.004$ [m]

$L = N_c \cdot c_p + 2 \cdot L_{ep}$

$W = \sqrt{A_c \cdot A_r}$ *width of stack assuming a square*

$b = 0.002$ [m^2]

$A_r = 1.2 + 0.05 \cdot \left[\frac{b}{A_c}\right]^2$

$Vol = c_f \cdot A_c \cdot A_r \cdot L$

$c_f = 1000$ [L/m^3]

volume is not very sensitive to the stack voltage

Choose 12 V because the aspect ratio of stack at high voltage is severe, likely hard to manufacture and hard to package

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$A = 0.0625$ [m^2]	$A_c = 0.002083$ [m^2]
$A_r = 1.246$	$b = 0.002$ [m^2]
$c_f = 1000$ [L/m^3]	$c_p = 0.004$ [m]
$i = 2000$ [A/m^2]	$L = 0.135$ [m]
$L_{ep} = 0.0075$ [m]	$N_c = 30$
$P = 50$ [W]	$V_{cell} = 0.4$ [V]
$Vol = 0.3505$ [L]	$V_s = 12$ [V]
$W = 0.05095$ [m]	

No unit problems were detected.

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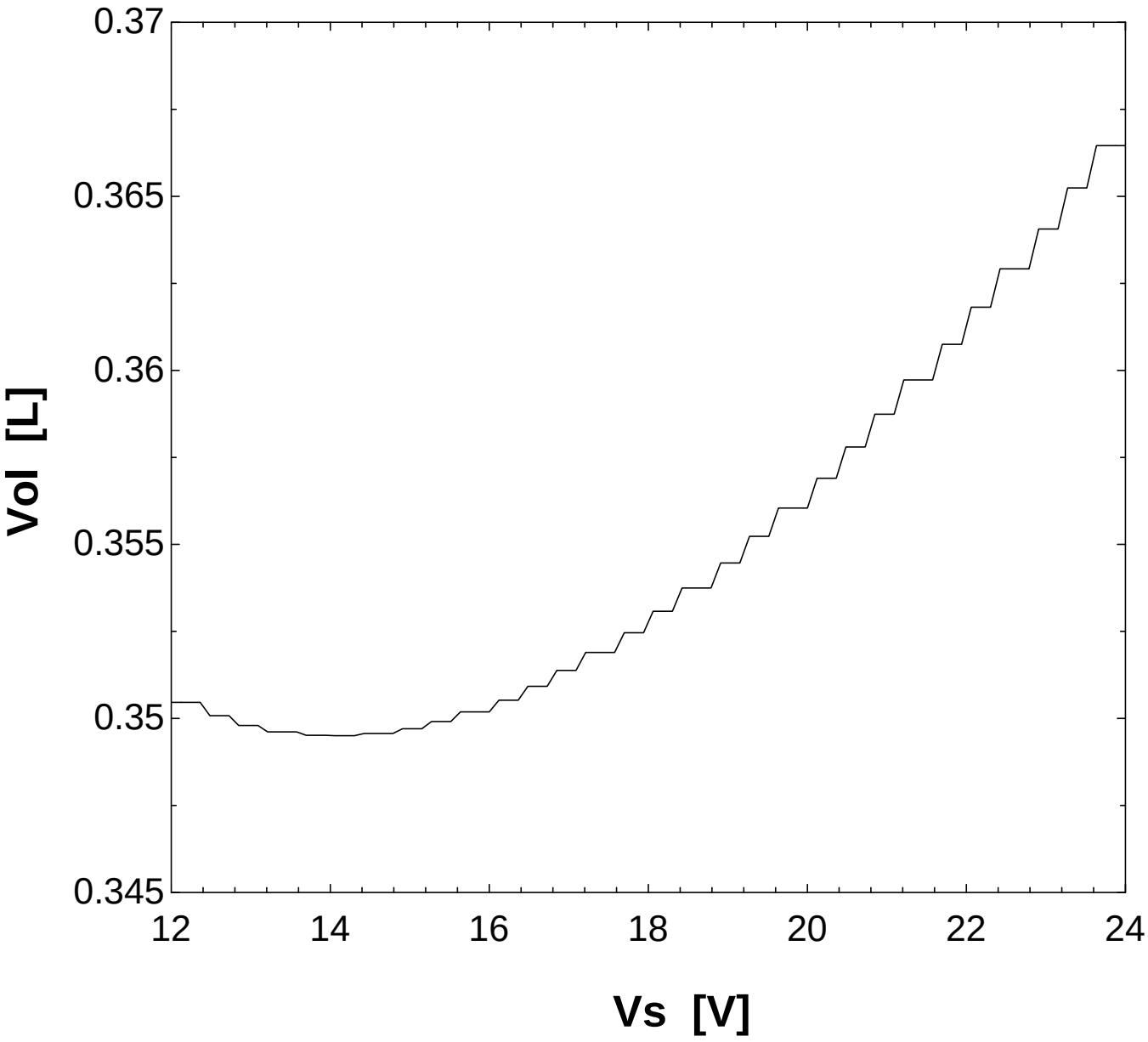

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PROBLEM 10-9

$R = 8.314$ [J/mol-K]

$F = 96485$ [coulomb/mol]

$n = 4$

$T1 = 353$ [K]

$p1 = 100000$ [Pa]

$pw = \mathbf{P}_{sat}[\text{water}, T = T1]$

$yod = 0.21$ *mole fraction oxygen on dry basis, air is 21 % oxygen*

$yw = \frac{pw}{p1}$ *mole fraction water*

partial pressure of oxygen

$p_{O2} = p1 \cdot yod \cdot [1 - yw] \cdot [1 - u]$

u=0.3

utilization of oxgyen

$Deff = 0.000006$ [m^2/s]

$L = 0.00017$ [m]

$I_{lim} = n \cdot F \cdot Deff \cdot \frac{p_{O2}}{L \cdot R \cdot T1}$

SOLUTION

Unit Settings: SI K Pa J molar deg

(Table 1, Run 100)

Deff = 0.000006 [m^2/s]	F = 96485 [coulomb/mol]
I_{lim} = 15472 [A/m^2]	L = 0.00017 [m]
n = 4	p1 = 100000 [Pa]
pw = 47086 [Pa]	p_{O2} = 3334 [Pa]
R = 8.314 [J/mol-K]	T1 = 353 [K]
u = 0.7	yod = 0.21
yw = 0.4709	

No unit problems were detected.

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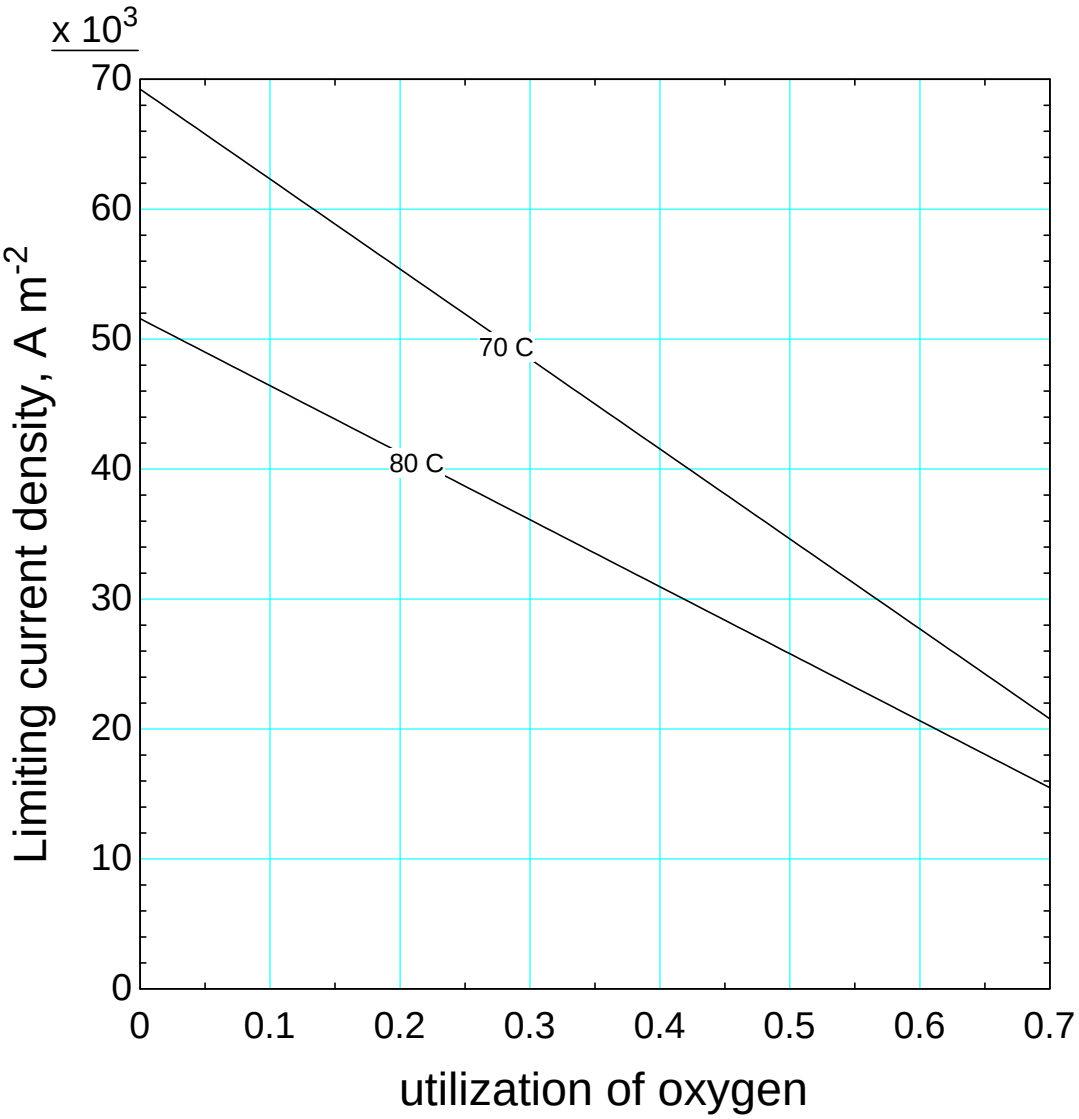
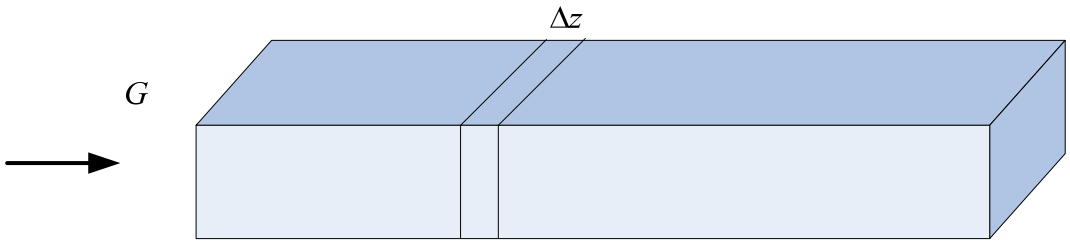


When analyzing the performance of a low temperature fuel cell, it is often desirable to include the effect of oxygen utilization with a one-dimensional analysis. If the mole fraction of oxygen changes across the electrode, what value should be used? Assuming that the oxygen reduction reaction is *first order* in oxygen concentration, show that it is appropriate to use a log-mean mole fraction of oxygen as an approximation of the average mole fraction.

$$y_{\text{lm}} \equiv \frac{y_{\text{in}} - y_{\text{out}}}{\ln \frac{y_{\text{in}}}{y_{\text{out}}}}$$



Assume a total molar flowrate per unit width, *G*, is constant. Perform a mass balance on oxygen over a differential length, Δz. *y* is the mole fraction of oxygen.

in-out=consumption

$$GWy|_z - GWy|_{z+\Delta z} = kyW\Delta z$$

$$\frac{dy}{dz} = -\frac{ky}{G}$$

$$\int_{y_i}^{y_o} \frac{dy}{y} = \frac{k}{G}\int_{L}^{0} dz$$

$$\ln \frac{y_i}{y_o} = \frac{kL}{G}$$

Overall balance on oxygen, amount consumed is

$$GW(y_i - y_o)$$

y_i is the mole fraction of oxygen entering. We can define the average current density in terms of oxygen consumed based on the stoichiometry of the reaction

$$i_{avg} = \frac{nFGW(y_i - y_o)}{LW}$$

substitute $G = \frac{kL}{\ln \frac{y_i}{y_o}}$

$$i_{avg} = \frac{nFk(y_i - y_o)}{\ln \frac{y_i}{y_o}}$$

$$i_{avg} = nFKy_{lm}$$

Express the log-mean term in Problem 10-10 in terms of oxygen utilization and the inlet mole fraction of oxygen, y_{in}. Sketch the average current density as a function of utilization, keeping the overpotential for oxygen reduction fixed. How would this change if mass transfer is also included.

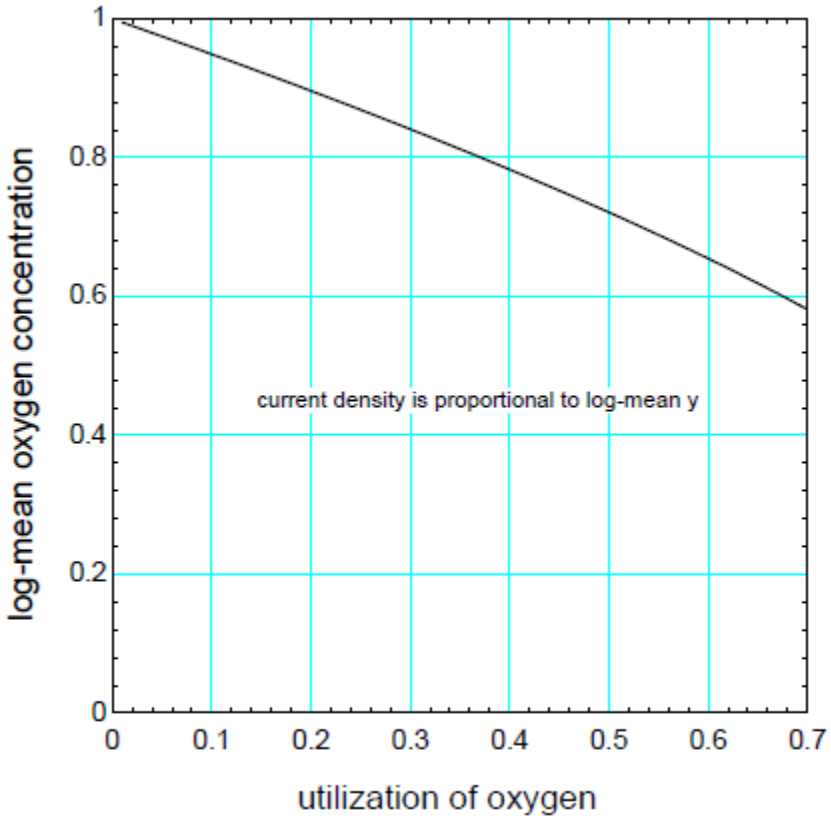
$$u = \frac{\text{in} - \text{out}}{\text{in}} = \frac{y_i - y_o}{y_i}$$

Thus

$$\frac{y_o}{y_i} = 1 - u$$

$$y_{lm} = \frac{(y_i - y_o)}{\ln \frac{y_i}{y_o}} = \frac{u y_i}{\ln\left(\frac{1}{1-u}\right)} = \frac{-u y_i}{\ln(1-u)}$$

the average current density is proportional to y_{lm}. The plot shows that the average current density decreases at a fixed overpotential. Mass transfer would make the effect of utilization even greater.



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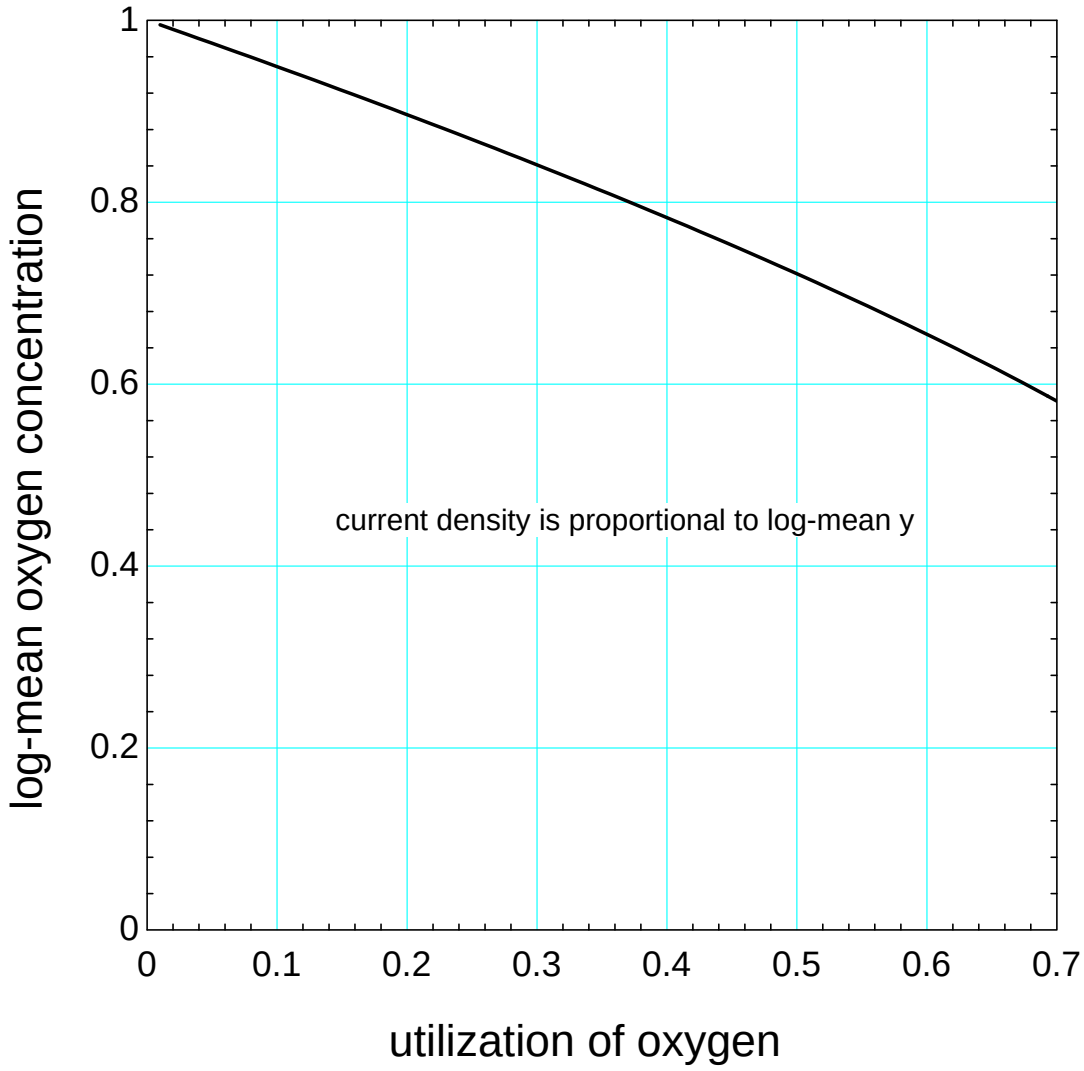
PROBLEM 10-11

$$y = \frac{-u}{\ln[1-u]}$$

$$x = 1 - u$$

x=0.2



We would expect that the two definitions would give similar, but not exactly the same, value.

$$\eta_{fp} = \frac{\text{rate in equivalents of oxidizable fuel supplied to stack}}{\text{rate in equivalents of fuel supplied to fuel processor}} \tag{10-24}$$

$$\eta_{fp} = \frac{\text{heating value of the fuel supplied to stack}}{\text{heating value of fuel supplied to fuel processor}},$$

The main advantage of the first definition, equation 10.24, is that we can obtain the fuel efficiency directly by multiplying by the utilization of fuel, which then can be used to calculate the thermal efficiency, equation 10.4. Utilization of fuel and fuel efficiencies are important design parameters; and maintaining the relationship between them is useful.

$$\eta_{fp} \times u_f = \frac{\text{rate in equivalents consumed in stack}}{\text{rate in equivalents of fuel supplied to fuel processor}} = \eta_{fuel}, \tag{10-25}$$

The alternative definition for fuel processing efficiency is conceptually simply and more familiar to many engineers, but it does not allow a straightforward use of equaiton 10.4 nor preserve the definition for utilization.

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PROBLEM 10-13

composition of fuel, mole fraction

$y_{CO2} = 0.007$

$y_{CH4} = 0.949$

$y_{eth} = 0.025$

$y_{prop} = 0.002$

$y_{but} = 0.0003$

$y_{N2} = 0.0167$

MW of fuel components

$m_{CO2} = 0.044$ [kg/mol]

$m_{CH4} = 0.016$ [kg/mol]

$m_{eth} = 0.0307$ [kg/mol]

$m_{prop} = 0.0441$ [kg/mol]

$m_{but} = 0.05812$ [kg/mol]

$m_{N2} = 0.028$ [kg/mol]

enthalpy of combustion of fuel components, lower heating value

$h_{CO2} = 0$ [J/kg]

$h_{CH4} = 5.59 \times 10^7$ [J/kg]

$h_{eth} = 5.19 \times 10^7$ [J/kg]

$h_{prop} = 4.6296 \times 10^7$ [J/kg]

$h_{but} = 4.5277 \times 10^7$ [J/kg]

$h_{N2} = 0$ [J/kg]

Calculate mole fractions to mass fractions, basis of one total mole

$$w_{CO2} = y_{CO2} \cdot \left[\frac{m_{CO2}}{y_{CO2} \cdot m_{CO2} + y_{CH4} \cdot m_{CH4} + y_{eth} \cdot m_{eth} + y_{prop} \cdot m_{prop} + y_{but} \cdot m_{but} + y_{N2} \cdot m_{N2}} \right]$$

$$w_{CH4} = y_{CH4} \cdot \left[\frac{m_{CH4}}{y_{CO2} \cdot m_{CO2} + y_{CH4} \cdot m_{CH4} + y_{eth} \cdot m_{eth} + y_{prop} \cdot m_{prop} + y_{but} \cdot m_{but} + y_{N2} \cdot m_{N2}} \right]$$

$$w_{eth} = y_{eth} \cdot \left[\frac{m_{eth}}{y_{CO2} \cdot m_{CO2} + y_{CH4} \cdot m_{CH4} + y_{eth} \cdot m_{eth} + y_{prop} \cdot m_{prop} + y_{but} \cdot m_{but} + y_{N2} \cdot m_{N2}} \right]$$

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$$w_{prop} = y_{prop} \cdot \left[\frac{m_{prop}}{y_{CO2} \cdot m_{CO2} + y_{CH4} \cdot m_{CH4} + y_{eth} \cdot m_{eth} + y_{prop} \cdot m_{prop} + y_{but} \cdot m_{but} + y_{N2} \cdot m_{N2}} \right]$$

$$w_{but} = y_{but} \cdot \left[\frac{m_{but}}{y_{CO2} \cdot m_{CO2} + y_{CH4} \cdot m_{CH4} + y_{eth} \cdot m_{eth} + y_{prop} \cdot m_{prop} + y_{but} \cdot m_{but} + y_{N2} \cdot m_{N2}} \right]$$

$$w_{N2} = y_{N2} \cdot \left[\frac{m_{N2}}{y_{CO2} \cdot m_{CO2} + y_{CH4} \cdot m_{CH4} + y_{eth} \cdot m_{eth} + y_{prop} \cdot m_{prop} + y_{but} \cdot m_{but} + y_{N2} \cdot m_{N2}} \right]$$

Determine LHV of fuel per mass

$$LHV = w_{CO2} \cdot h_{CO2} + w_{CH4} \cdot h_{CH4} + w_{eth} \cdot h_{eth} + w_{prop} \cdot h_{prop} + w_{but} \cdot h_{but} + w_{N2} \cdot h_{N2}$$

calculate effciciencies

$u_f = 0.8$

$\eta_{fp} = 0.78$

$\eta_{vt} = 0.6$

$\eta_{mech} = 0.92$

$\eta_{powcond} = 0.96$

$\eta_{fuel} = u_f \cdot \eta_{fp}$

$\eta_{th} = \eta_{fp} \cdot u_f \cdot \eta_{vt} \cdot \eta_{powcond} \cdot \eta_{mech}$

connect to conditioned power

$P = 400000$ [W]

$$\eta_{th} = \frac{P}{\dot{m} \cdot LHV}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$\eta_{fp} = 0.78$
$\eta_{mech} = 0.92$
$\eta_{th} = 0.3307$
$h_{but} = 4.528E+07$ [J/kg]
$h_{CO2} = 0$ [J/kg]
$h_{N2} = 0$ [J/kg]
$LHV = 5.308E+07$ [J/kg]
$m_{CH4} = 0.016$ [kg/mol]
$\dot{m} = 0.02279$ [kg/s]
$m_{N2} = 0.028$ [kg/mol]
$P = 400000$ [W]
$w_{but} = 0.001036$
$w_{CO2} = 0.0183$
$w_{N2} = 0.02778$
$\eta_{fuel} = 0.624$
$\eta_{powcond} = 0.96$
$\eta_{vt} = 0.6$
$h_{CH4} = 5.590E+07$ [J/kg]
$h_{eth} = 5.190E+07$ [J/kg]
$h_{prop} = 4.630E+07$ [J/kg]
$m_{but} = 0.05812$ [kg/mol]
$m_{CO2} = 0.044$ [kg/mol]
$m_{eth} = 0.0307$ [kg/mol]
$m_{prop} = 0.0441$ [kg/mol]
$u_f = 0.8$
$w_{CH4} = 0.9021$
$w_{eth} = 0.0456$
$w_{prop} = 0.00524$

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y_{but} = 0.0003
y_{CO2} = 0.007
y_{N2} = 0.0167
y_{CH4} = 0.949
y_{eth} = 0.025
y_{prop} = 0.002

No unit problems were detected.

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PROBLEM 10-14a

based on air as reactant, assumes parallel flow fields

Input data

$w = 0.002$ [m] *channel width*

$h = 0.002$ [m] *channel height*

$rib = 0.003$ [m] *rib width*

$u = 0.55$ *utilization of reactant*

$n = 4$ *four electrons per O2 molecule based on simple stoichiometry*

$y = 0.21$ *21 % oxygen*

$MW = 0.029$ [kg/mol] *molecular weight of air*

$Tc = 75$ [C] *temperature of operation*

$pc = 100$ [kPa]

$po = \mathbf{P}_{sat}[\text{water}, T = Tc]$

$I = 16000$ [A/m^2] *average current density*

$F = 96485$ [Coulomb/mol]

$pw = 0.24$ [m] *planform width*

$ph = 0.12$ [m] *planform length, that is along direction of flow*

determine flowrate of air needed and velocity in channel

$\rho = \rho[\text{Air}, T = Tc, P = pc]$

$$Q = pw \cdot ph \cdot I \cdot \left[\frac{\frac{MW}{n \cdot F \cdot y \cdot \rho}}{1 - \frac{po}{pc}} \right]$$ *volumetric flow of air and water*

$$Q = V \cdot pw \cdot h \cdot \left[\frac{w}{w + rib} \right]$$ *assumes single channel*

calculate Reynolds number

$\mu = \mathbf{Visc}[\text{Air}, T = Tc]$

$$Dh = 4 \cdot w \cdot \frac{h}{2 \cdot [w + h]}$$

$$Re = \rho \cdot Dh \cdot \frac{V}{\mu}$$

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ASSUMING LAMINAR FLOW

determine pressure drop in channel that is length L

$$L = ph$$

$$hl = \frac{2 \cdot fan \cdot \frac{L}{Dh} \cdot V \cdot V}{9.807 \ [m/s^2]}$$

$$DP = hl \cdot \rho \cdot 9.807 \ [m/s^2]$$

$$fan = \frac{16}{Re}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

Dh = 0.002 [m]
F = 96485 [Coulomb/mol]
h = 0.002 [m]
I = 16000 [A/m^2]
μ = 0.00002074 [Pa-s]
n = 4
ph = 0.12 [m]
pw = 0.24 [m]
Re = 134.8
rib = 0.003 [m]
u = 0.55
w = 0.002 [m]

DP = 27.81 [Pa]
fan = 0.1187
hl = 2.834 [m]
L = 0.12 [m]
MW = 0.029 [kg/mol]
pc = 100 [kPa]
po = 38.56 [kPa]
Q = 0.0002682 [m^3/s]
ρ = 1.001 [kg/m^3]
Tc = 75 [C]
V = 1.397 [m/s]
y = 0.21

No unit problems were detected.

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PROBLEM 10-14b

based on air as reactant, assumes small number of serpentine flow fields

ns = 3

Input data

w = 0.002 [m] *channel width*

h = 0.002 [m] *channel height*

rib = 0.003 [m] *rib width*

u = 0.55 *utilization of reactant*

n = 4 *four electrons per O2 molecule based on simple stoichiometry*

y = 0.21 *21 % oxygen*

MW = 0.029 [kg/mol] *molecular weight of air*

Tc = 75 [C] *temperature of operation*

pc = 100 [kPa]

po = $\mathbf{P}_{sat}$ [water , T = Tc]

I = 16000 [A/m^2] *average current density*

F = 96485 [Coulomb/mol]

pw = 0.24 [m] *planform width*

ph = 0.12 [m] *planform length, that is along direction of flow*

determine flowrate of air needed and velocity in channel

$\rho = \rho$[Air , T = Tc , P = pc]

$$Q = pw \cdot ph \cdot I \cdot \left[\frac{\frac{MW}{n \cdot F \cdot y \cdot \rho}}{1 - \frac{po}{pc}} \right]$$ *volumetric flow of air and water*

Q = V · w · h · ns *assumes single channel*

calculate Reynolds number

μ = **Visc** [Air , T = Tc]

$$Dh = 4 \cdot w \cdot \frac{h}{2 \cdot [w + h]}$$

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$$Re = \rho \cdot Dh \cdot \frac{V}{\mu}$$

ASSUMING LAMINAR FLOW

determine pressure drop in channel that is length L

$$L = ph \cdot \left[\frac{pw}{w + rib}\right]$$

$$hl = \frac{2 \cdot fan \cdot \frac{L}{Dh} \cdot V \cdot V}{9.807 \ [m/s^2]}$$

$$DP = hl \cdot \rho \cdot 9.807 \ [m/s^2]$$

$$fan = \frac{16}{Re}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

Dh = 0.002 [m]
F = 96485 [Coulomb/mol]
h = 0.002 [m]
I = 16000 [A/m^2]
μ = 0.00002074 [Pa-s]
n = 4
pc = 100 [kPa]
po = 38.56 [kPa]
Q = 0.0002682 [m^3/s]
ρ = 1.001 [kg/m^3]
Tc = 75 [C]
V = 22.35 [m/s]
y = 0.21

DP = 21359 [Pa]
fan = 0.007419
hl = 2176 [m]
L = 5.76 [m]
MW = 0.029 [kg/mol]
ns = 3
ph = 0.12 [m]
pw = 0.24 [m]
Re = 2157
rib = 0.003 [m]
u = 0.55
w = 0.002 [m]

No unit problems were detected.

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PROBLEM 10-15

nominal quantities

$a = 0.0015$ [m]

$b = 0.002$ [m]

$$Dh = 2 \cdot \left[\frac{a \cdot b}{a + b} \right]$$

$U_{nom} = 0.55$ *utilization*

$U_{tol} = 0.65$ *worst case utilization*

$c = a \cdot r$ *dimensions allowed*

$d = b \cdot r$ *dimension allowed*

$$Dt = 2 \cdot \left[\frac{c \cdot d}{c + d} \right]$$

$$Q_{ratio} = \frac{a^3 \cdot \frac{b^3}{[a + b]^2}}{c^3 \cdot \frac{d^3}{[c + d]^2}}$$

$U_{tol} = Q_{ratio} \cdot U_{nom}$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$a = 0.0015$ [m]	$b = 0.002$ [m]
$c = 0.001439$ [m]	$d = 0.001918$ [m]
$Dh = 0.001714$ [m]	$Dt = 0.001644$ [m]
$Q_{ratio} = 1.182$	$r = 0.9591$
$U_{nom} = 0.55$	$U_{tol} = 0.65$

No unit problems were detected.

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PROBLEM 10-16

Effect of pressure

F = 96485 [Coulomb/mol]

u, oxidant utilization

yo, mole fraction oxgyen in air

yox = 0.21

Tc, cell temperature, K

Tc=310 [K]

mole fraction water in air entering

y1 = 0

y2, mole fraction of water exiting

$$y2 = \frac{p2}{p}$$

p = 300000 [Pa]

$$p2 = \mathbf{P}_{sat}\left[\text{water}, T = Tc\right]$$

water balance, neglecting water removed from anode

$$2 \cdot u \cdot yox + \frac{y1}{1 - y1} = \left[1 - u \cdot yox\right] \cdot \left[\frac{y2}{1 - y2}\right]$$

with increasing pressure, less water is removed with the spent air. It is more likely that liquid water will be present if the utilization is fixed. Pressure does allow the cell to be operated at a higher temperature without concern for dryout.

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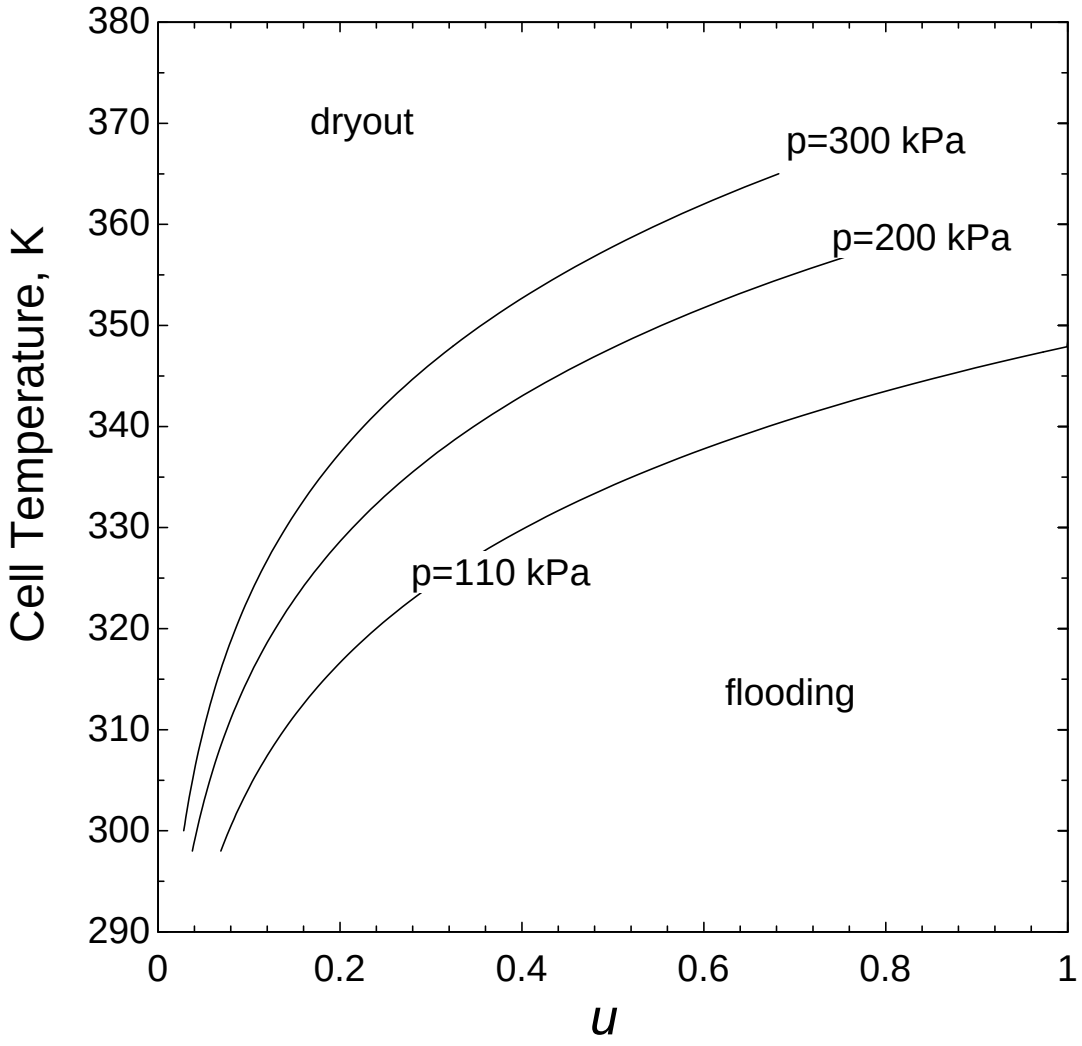

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PROBLEM 10-17

current density

$I = 10000$ [A/m^2]

$F = 96485$ [Coulomb/mol]

$n = 4$ *four electrons per mole O2*

$$W = \frac{\frac{I}{n \cdot F}}{u \cdot yox}$$ *entering air flow*

u, oxidant utilization

yo, mole fraction oxgyen in air

$yox = 0.21$

Tc, cell temperature, K

$Tc = 328$ [K]

mole fraction water in air entering

$y1 = 0$

y2, mole fraction of water exiting

$$y2 = \frac{p2}{p}$$

$p = 120000$ [Pa]

$p2 = \mathbf{P}_{sat}[water, T = Tc]$

water balance, neglecting water removed from anode, Nw is amount of liquid water removed

$$2 \cdot u \cdot yox \cdot W + W \cdot \left[\frac{y1}{1 - y1}\right] = W \cdot [1 - u \cdot yox] \cdot \left[\frac{y2}{1 - y2}\right] + 2 \cdot Nw$$

$u = 0.4$

water balance is achieved at 33 % oxygen utilization, therefore some water must be removed as liquid

fraction

$$Lf = 2 \cdot \frac{Nw}{\frac{I}{2 \cdot F}}$$

SOLUTION

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Unit Settings: SI K Pa J molar deg

F = 96485 [Coulomb/mol]
I = 10000 [A/m^2]
Lf = 0.1829
n = 4
Nw = 0.00474 [mol/m^2-s]
p = 120000 [Pa]
p2 = 15639 [Pa]
Tc = 328 [K]
u = 0.4
W = 0.3085 [mol/m^2-s]
y1 = 0
y2 = 0.1303
yox = 0.21

No unit problems were detected.

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PROBLEM 10-18

energy balance to relate temperature of cell to air stoichiometry

assume we start with 1 mol/s methane, and Wa mol/s air

Wa obtained from two definitions of utilization

Wf = 0.0001 [kmol/s] *assumed as basis*

Wa · yo · uo = Wf · uf · 2 *stoichiometry of overall reaction*

mole fraction oxygen in air

yo = 0.21

pc = 110 [kPa]

Tg = 900 [C]

species 1, hydrogen

c1 = **Cp** [Hydrogen , P = pc , T = Tg]

hf1 = 0 [J/kmol]

species, 2 water

c2 = **Cp** [water , P = pc , T = Tg]

hf2 = – 2.4182 x 10^{8} [J/kmol]

species 3 air

c3 = **Cp** [Air , T = Tg]

hf3 = 0 [J/kmol]

species 4 CO

c4 = **Cp** [CarbonMonoxide , P = pc , T = Tg]

hf4 = – 1.1053 x 10^{8} [J/kmol]

species 5 CO2

c5 = **Cp** [CarbonDioxide , P = pc , T = Tg]

hf5 = – 3.9351 x 10^{8} [J/kmol]

utilizations

uf represents utilization of both CO and H2

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uf = 0.9

specifiy potential of individual cell, Vc

Vc = 0.7 [V]

let xi be the extent of water gas shift reaction

ξ = 0.3

sc is steam to carbon ratio

sc = 2.5

in1 = Wf · [3 + ξ]

out1 = Wf · [1 – uf] · [3 + ξ]

in2 = Wf · sc

prod2 = in1 · uf

out2 = sc · Wf + prod2

in3 = Wa

out3 = Wa · [1 – uo · yo]

in4 = Wf · [1 – ξ]

out4 = Wf · [1 – ξ] · [1 – uf]

in5 = Wf · ξ

out5 = Wf · [ξ + (1 – ξ) · uf]

overall energy balance, in-out=generation

Tc = 900 [C]

Ta = Tc – ΔT

ΔT = 200 [C]

Ein = [in1 · c1 + in2 · c2 + in4 · c4 + in5 · c5] · Tc + Wa · c3 · Ta

Eout = [out1 · c1 + out2 · c2 + out3 · c3 + out4 · c4 + out5 · c5] · Tc

Ep = yo · uo · Wa · 4 · 9.649E+07 [Coulomb/kmol] · Vc

heat generated from chemical reactions
calculated from heats of formation

dH = [in2 – out2] · hf2 + [in4 – out4] · hf4 + [in5 – out5] · hf5

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$$0 = \frac{Ein + dH - Eout - Ep}{Ein}$$

SOLUTION

Unit Settings: SI C kPa J molar deg

c1 = 30875 [J/kmol-C]
c2 = 43458 [J/kmol-C]
c3 = 33901 [J/kmol-C]
c4 = 29558 [J/kmol-C]
c5 = 56113 [J/kmol-C]
ΔT = 200 [C]
dH = 89648 [J/s]
Ein = 168072 [J/s]
Eout = 209091 [J/s]
Ep = 48629 [J/s]
hf1 = 0 [J/kmol]
hf2 = -2.418E+08 [J/kmol]
hf3 = 0 [J/kmol]
hf4 = -1.105E+08 [J/kmol]
hf5 = -3.935E+08 [J/kmol]
in1 = 0.00033 [kmol/s]
in2 = 0.00025 [kmol/s]
in3 = 0.006142 [kmol/s]
in4 = 0.00007 [kmol/s]
in5 = 0.00003 [kmol/s]
out1 = 0.000033 [kmol/s]
out2 = 0.000547 [kmol/s]
out3 = 0.005962 [kmol/s]
out4 = 0.000007 [kmol/s]
out5 = 0.000093 [kmol/s]
pc = 110 [kPa]
prod2 = 0.000297 [kmol/s]
sc = 2.5
Ta = 700 [C]
Tc = 900 [C]
Tg = 900 [C]
uf = 0.9
uo = 0.1396
Vc = 0.7 [V]
Wa = 0.006142 [kmol/s]
Wf = 0.0001 [kmol/s]
ξ = 0.3
yo = 0.21

No unit problems were detected.

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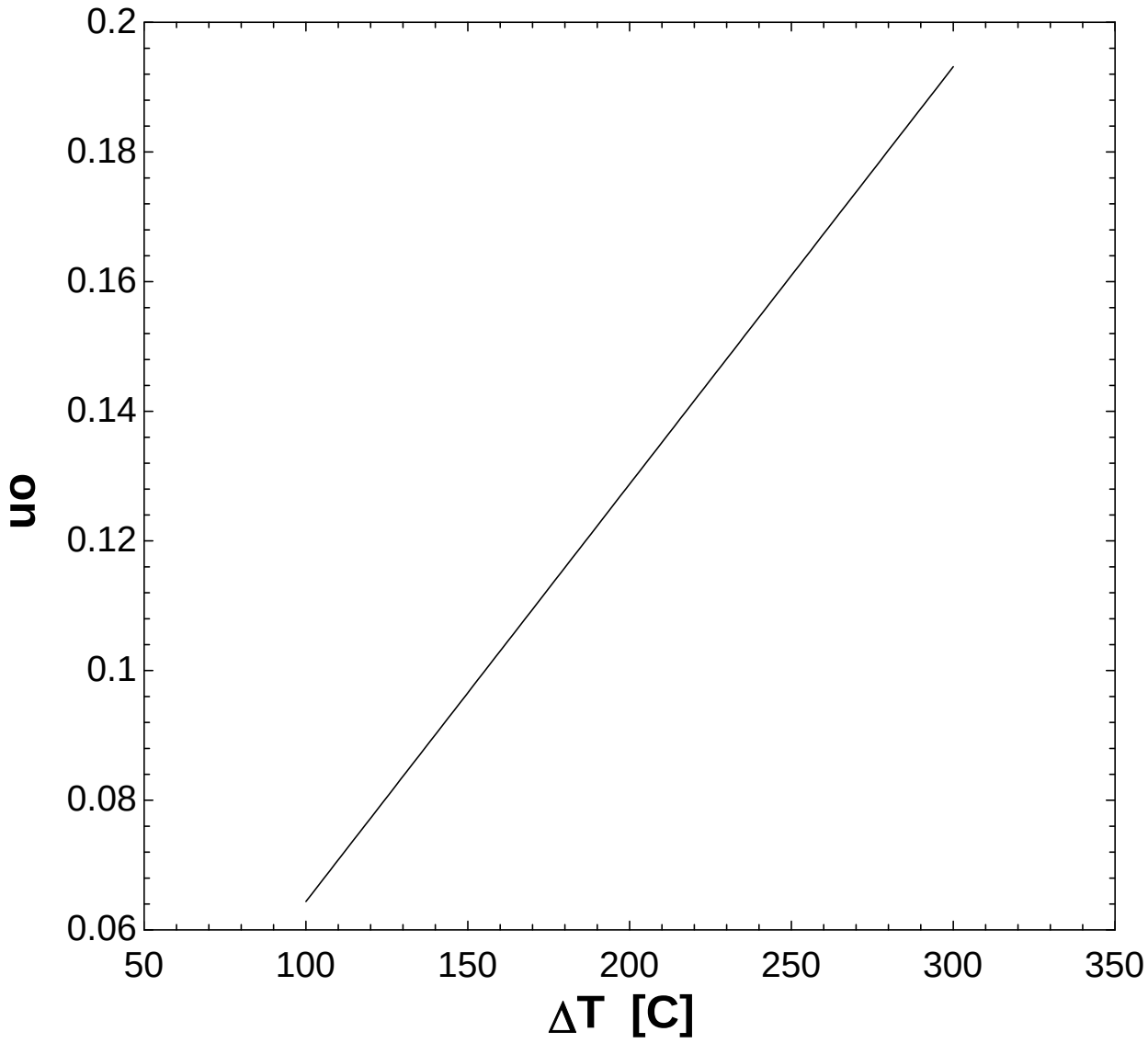

One of the simplest models for the cell voltage of a low-temperature hydrogen/oxygen fuel cell is

$$V = U + \frac{RT}{F}\ln\left[\frac{p_{O_2}\sqrt{p_{H_2}}}{i}\right] - R_\Omega i.$$

Using this model, which neglects mass transfer, how does the cell voltage change with oxygen utilization if the average current density is fixed? You may assume that the equilibrium potential, *U*, is constant. You will need to use an average oxygen partial pressure that accounts for the change in oxygen concentration along the length of the electrode.

$$\frac{F\Delta V}{RT} = \ln\frac{p_{O_2}^{in}}{p_{O_2}^{u}}$$

where the superscript u indicates the average partial pressure with utilization, u. Use the log-mean average to quantify this effect, problem 10-10.

$$p_{O_2}^{u} = \frac{p(y_i - y_{out})}{\ln\frac{y_{in}}{y_{out}}} = \frac{p y_{O_2} u}{\ln\left(\frac{1}{1-u}\right)}$$

$$\frac{F\Delta V}{RT} = \ln\left\{\frac{-\ln(1-u)}{u}\right\}$$

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PROBLEM 10-20

specifications

$y_{in} = 0.9$ *inlet concentration of feed*

$u_{fs} = 0.9$ *overall utilization*

u_f=0.5

utilization in stack

R=1.5

$wr = 1$ [mol/s] *arbitrary basis*

definitions

$$u_f = \frac{ys \cdot [wr + wf] - \left[y \cdot (1 - ys) \cdot \left(\frac{wr + wf}{1 - y}\right)\right]}{ys \cdot [wr + wf]}$$ *stack utilization*

$$u_{fs} = \frac{wf \cdot y_{in} - wo \cdot y}{wf \cdot y_{in}}$$ *system utilizaiton*

$$R = \frac{wr}{wf}$$ *recycle ratio*

balances

$[1 - y_{in}] \cdot wf = wo \cdot [1 - y]$ *overall inerts*

$y_{in} \cdot wf + wr \cdot y = [wf + wr] \cdot ys$ *hydrogen at T*

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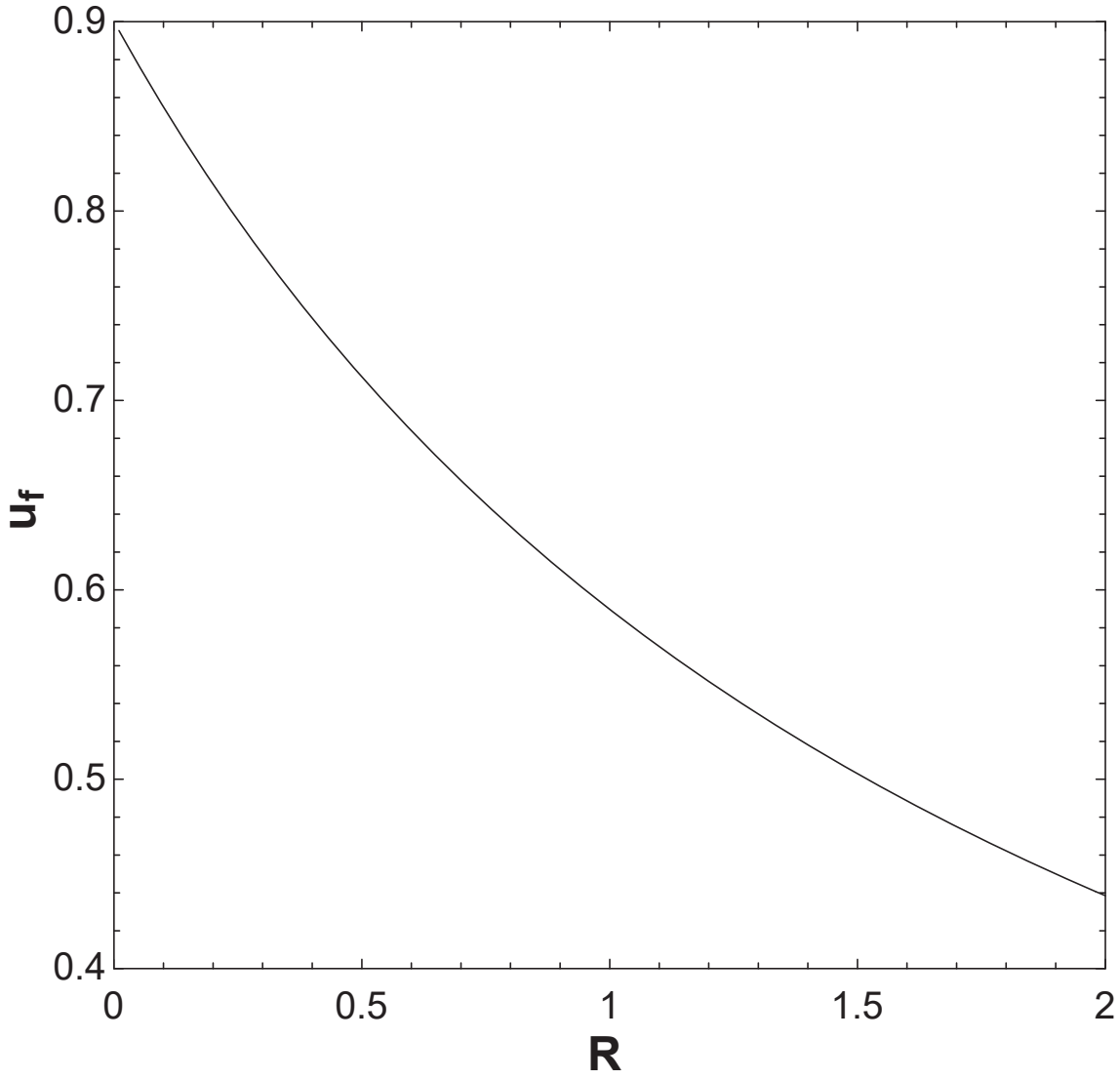

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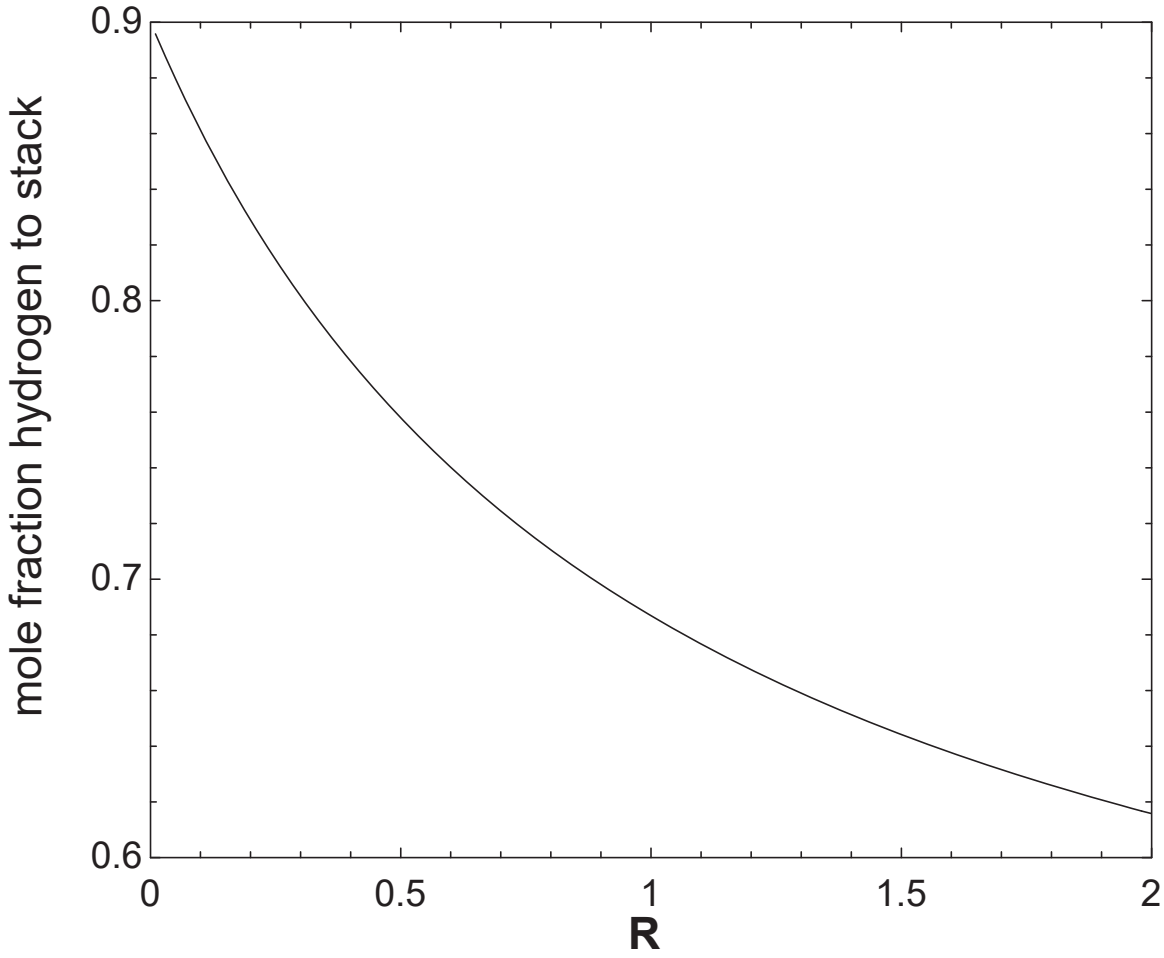

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PROBLEM 10-21

$L1 = 0.00017$ [m]

$e1 = 0.7$

$L2 = 0.0001$ [m]

$L1 \cdot [1 - e1] = L2 \cdot [1 - e2]$ *assumes density of solid is constant*

assume Bruggeman behavior

$$ratio = \left[\frac{e2}{e1}\right]^{1.5}$$

SOLUTION

Unit Settings: SI C kPa J mass deg

e1 = 0.7
L1 = 0.00017 [m]
ratio = 0.5857

e2 = 0.49
L2 = 0.0001 [m]

No unit problems were detected.

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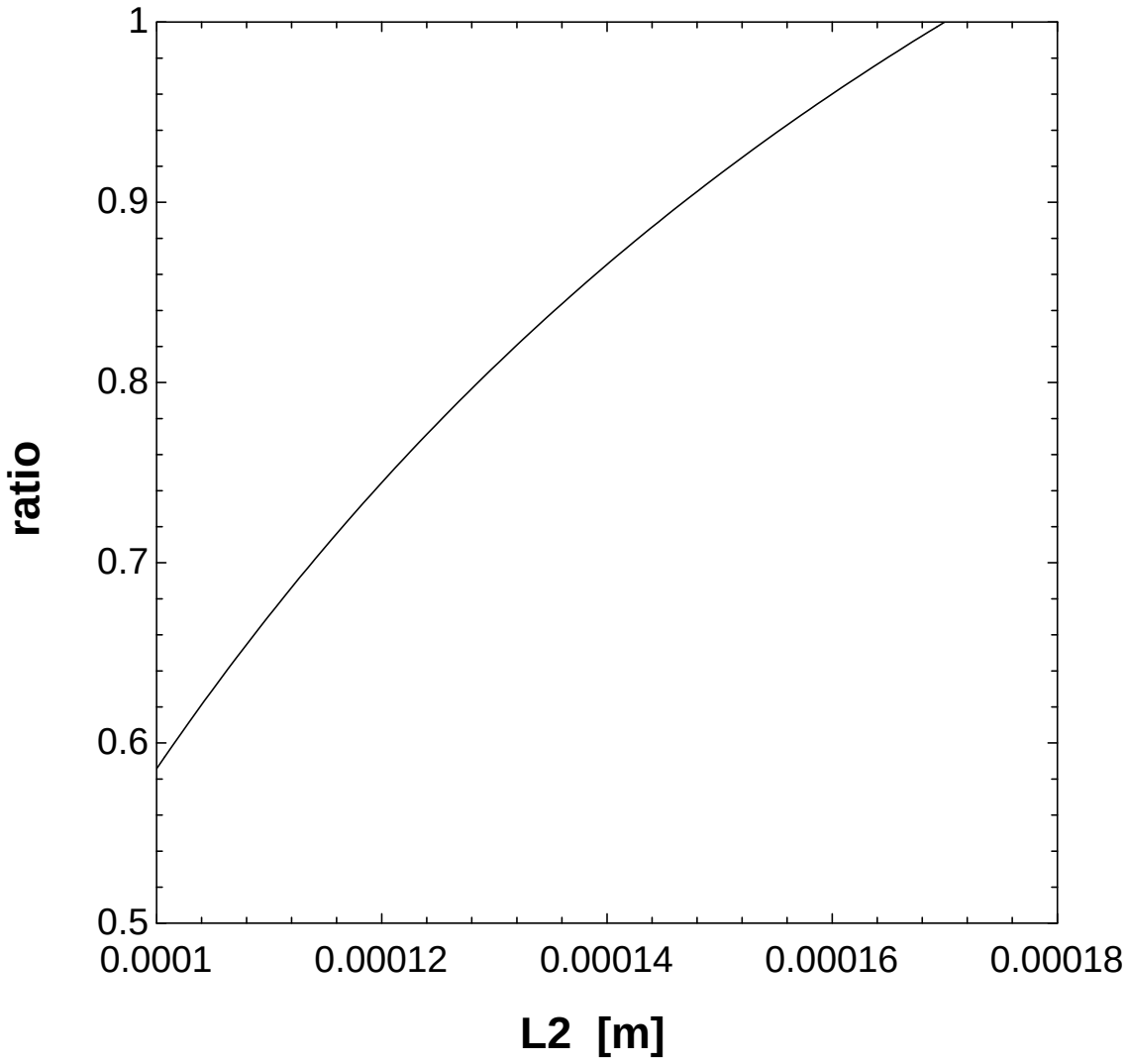


In the study of fuel consumption and utilization, several factors were neglected. Specifically, there can be leakage or permeation across the separator of a fuel cell. Additionally, there may be small shorts due, for instance, to the small electronic conductivity of a SOFC electrolyte or a small ionic conductivity in the interconnects (bipolar plates). Briefly discuss how these factors would affect the design of a fuel-cell system and propose a definition for the fuel utilization that accounts for these additional factors.

Use hydrogen as an example, Equation 10-19

$$u_f \equiv \frac{\text{rate of hydrogen consumption}}{\text{rate of hydrogen being supplied}} = \frac{(i/nF)A}{\dot{m}_f y_{H_2}/M_f} \tag{10-19}$$

This equation assumes that all of the hydrogen consumption occurs through the desired faradaic reaction and that there are no internal shorts.

The cell could have an electrical short as well as a chemical short, fuel permeation across the separator. Both would consume fuel but would not show up in the external current measured.

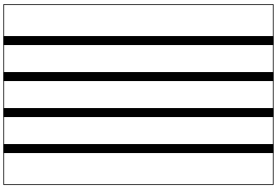
revised definition, A_c is the cross sectional area of a cell and N_c is the number of cells in the stacak

$$u_f{}^* \equiv \frac{\text{fardaic+short+fuel crossover}}{\text{rate of hydrogen being supplied}}$$

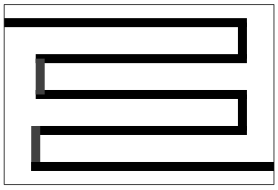
$$u_f{}^* \equiv \frac{(i/nF)A_cN_c+(I_{short}/nF)N_c+J_{fuel}A_cN_c}{\dot{m}_f y_{H_2}/M_f}$$

where J_{fuel} is the molar flux of fuel crossover

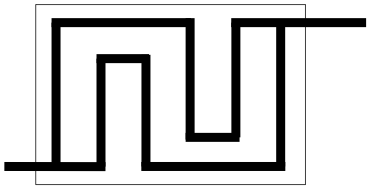
Problem 10.23



straight through parallel

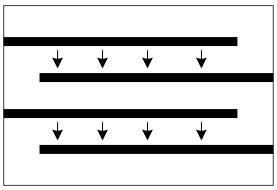


serpentine



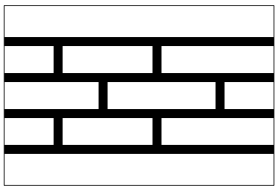
parallel serpentine

in

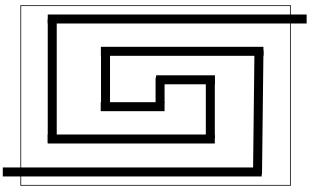


out

interdigitated



mesh



spiral

Key considerations are pressure drop, flow maldistribution, and utilization effects. The straight through parallel and serpentine provide two extreme examples. The straight through parallel provides multiple paths for the fluid, which results in lower velocities and shorter lengths, and thus lower pressure drop. The disadvantage of this design is that if the channels are not identical, flow through the channels can vary significantly, see Figure 10.13. The serpentine has only one channels, but now the length is much larger and the velocity much higher, resulting in much greater pressure drop. The parallel serpentine and mesh designs fall in between the two extremes, trying to balance pressure drop and better distribution of reactants. The interdigitated design forces flow from the inlet channel through the gas diffusion layer to an outlet channel. This improves the rate of mass transfer to the electrode, but again at the expense or pressure drop.

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PROBLEM 10-24

$F = 96485$ [coulomb/mol]

$nh = 2$

$no = 4$

$V_s = 42$ [V]

$Vcell = 0.6$ [V]

$V_s = Vcell \cdot Nc$

$I_{load} = 6000$ [A/m^2]

$P = 75000$ [W]

$P = Vcell \cdot I_{load} \cdot Ac \cdot Nc$

part b

$$Wh = I_{load} \cdot Nc \cdot \frac{Ac}{nh \cdot F}$$ *hydrogen flowrate*

$Mh = 2$ [g/mol]

$\dot{m}h = Wh \cdot Mh$

$$Wo = I_{load} \cdot Nc \cdot \frac{Ac}{no \cdot F}$$ *oxygen flow rate*

$Ma = 29$ [g/mol]

$y_o = 0.29$

$$\dot{m}a = Wo \cdot \frac{Ma}{y_o}$$ *air flowrate*

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$Ac = 0.2976$ [m^2]
$I_{load} = 6000$ [A/m^2]
$\dot{m}a = 32.39$ [g/s]
$\dot{m}h = 1.296$ [g/s]
$nh = 2$
$P = 75000$ [W]
$V_s = 42$ [V]
$Wo = 0.3239$ [mol/s]

$F = 96485$ [coulomb/mol]
$Ma = 29$ [g/mol]
$Mh = 2$ [g/mol]
$Nc = 70$
$no = 4$
$Vcell = 0.6$ [V]
$Wh = 0.6478$ [mol/s]
$y_o = 0.29$

No unit problems were detected.

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PROBLEM 10-25

water balance for integration of SR and SOFC

this example assumes that all exhaust gas is recycled to SR

Specify W1, SC, ufs

$$W1 = \frac{11}{16} \cdot 1 \quad [mol/s]$$ *moles methane feed*

$$SC = 2$$ *steam to carbon ratio*

ufs=0.85

overall fuel utiliztion

six variables, u, R, and four mole fractions exiting SOFC

$$y_{CO} = \frac{[1 - u] \cdot [W1 + W4 \cdot y_{CO}]}{Nt}$$

$$y_{CO2} = \frac{W4 \cdot y_{CO2} + u \cdot [W1 + W4 \cdot y_{CO}]}{Nt}$$

$$y_{H2} = \frac{[1 - u] \cdot [3 \cdot W1 + y_{H2} \cdot W4]}{Nt}$$

$$y_{H2O} = \frac{W4 \cdot y_{H2O} - W1 + u \cdot [3 \cdot W1 + y_{H2} \cdot W4]}{Nt}$$

$$Nt = [1 - u] \cdot [W1 + W4 \cdot y_{CO}] + W4 \cdot y_{CO2} + u \cdot [W1 + W4 \cdot y_{CO}] + [1 - u] \cdot [3 \cdot W1 + y_{H2} \cdot W4] + W4 \cdot y_{H2O} - W1 + u \cdot [3 \cdot W1 + y_{H2} \cdot W4]$$

$$R = \frac{W4}{W1}$$ *use inlet flow entering system in denominator*

*SC=W4*y_{H2O}/(W1+W4*($y_{CO+y,CO2}$)*

$$SC = W4 \cdot \frac{y_{H2O}}{W1}$$ *just use carbon in feed*

*uo=(W5*y_{CO2})/W1*

check=Y_{CO}+y_{CO2}+y_{H2}+y_{H2O}

$$ufs = \frac{W1 - W5 \cdot y_{CO}}{W1}$$

$$Nt = W4 + W5$$

Calculate the enthalpy in recycle stream

Assume that the exhaust is at 850 and the reformer at 550

As quick estimate use cp at 700 as average value

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$\Delta T = 300$ [K]

$Ta = [700 + 273] \cdot 1$ [K]

$Rg = 8.314$ [J/mol-K]

$a1 = 3.376$ *CO, data from de Nevers book*

$b1 = 0.000557$ [1/K]

$c1 = 0$ [$1/K^2$]

$d1 = -3100$ [K^2]

$$\frac{Cp1}{Rg} = a1 + b1 \cdot Ta + c1 \cdot Ta \cdot Ta + \frac{d1}{Ta \cdot Ta}$$

$a2 = 5.547$ *CO2*

$b2 = 0.001045$ [1/K]

$c2 = 0$ [$1/K^2$]

$d2 = -115700$ [K^2]

$$\frac{Cp2}{Rg} = a2 + b2 \cdot Ta + c2 \cdot Ta \cdot Ta + \frac{d2}{Ta \cdot Ta}$$

$a3 = 3.249$ *H2*

$b3 = 0.000422$ [1/K]

$c3 = 0$ [$1/K^2$]

$d3 = 8300$ [K^2]

$$\frac{Cp3}{Rg} = a3 + b3 \cdot Ta + c3 \cdot Ta \cdot Ta + \frac{d3}{Ta \cdot Ta}$$

$a4 = 3.47$ *H2O*

$b4 = 0.00145$ [1/K]

$c4 = 0$ [$1/K^2$]

$d4 = 12100$ [K^2]

$$\frac{Cp4}{Rg} = a4 + b4 \cdot Ta + c4 \cdot Ta \cdot Ta + \frac{d4}{Ta \cdot Ta}$$

$$\Delta H = R \cdot \Delta T \cdot [Cp1 \cdot y_{CO} + Cp2 \cdot y_{CO2} + Cp3 \cdot y_{H2} + Cp4 \cdot y_{H2O}]$$

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SOLUTION

Unit Settings: SI C kPa kJ mass deg

(Table 1, Run 100)

a1 = 3.376
a2 = 5.547
a3 = 3.249
a4 = 3.47
b1 = 0.000557 [1/K]
b2 = 0.001045 [1/K]
b3 = 0.000422 [1/K]
b4 = 0.00145 [1/K]
c1 = 0 [1/K^2]
c2 = 0 [1/K^2]
c3 = 0 [1/K^2]
c4 = 0 [1/K^2]
Cp1 = 32.55 [J/mol-K]
Cp2 = 53.56 [J/mol-K]
Cp3 = 30.5 [J/mol-K]
Cp4 = 40.69 [J/mol-K]
d1 = -3100 [K^2]
d2 = -115700 [K^2]
d3 = 8300 [K^2]
d4 = 12100 [K^2]
ΔH = 42924 [J/mol]
ΔT = 300 [K]
Nt = 4.292 [mol/s]
R = 3.243
Rg = 8.314 [J/mol-K]
SC = 2
Ta = 973 [K]
u = 0.9013
ufs = 0.95
W1 = 0.6875 [mol/s]
W4 = 2.23 [mol/s]
W5 = 2.063 [mol/s]
y_{CO} = 0.01667
y_{CO2} = 0.3167
y_{H2} = 0.05
y_{H2O} = 0.6167

No unit problems were detected.

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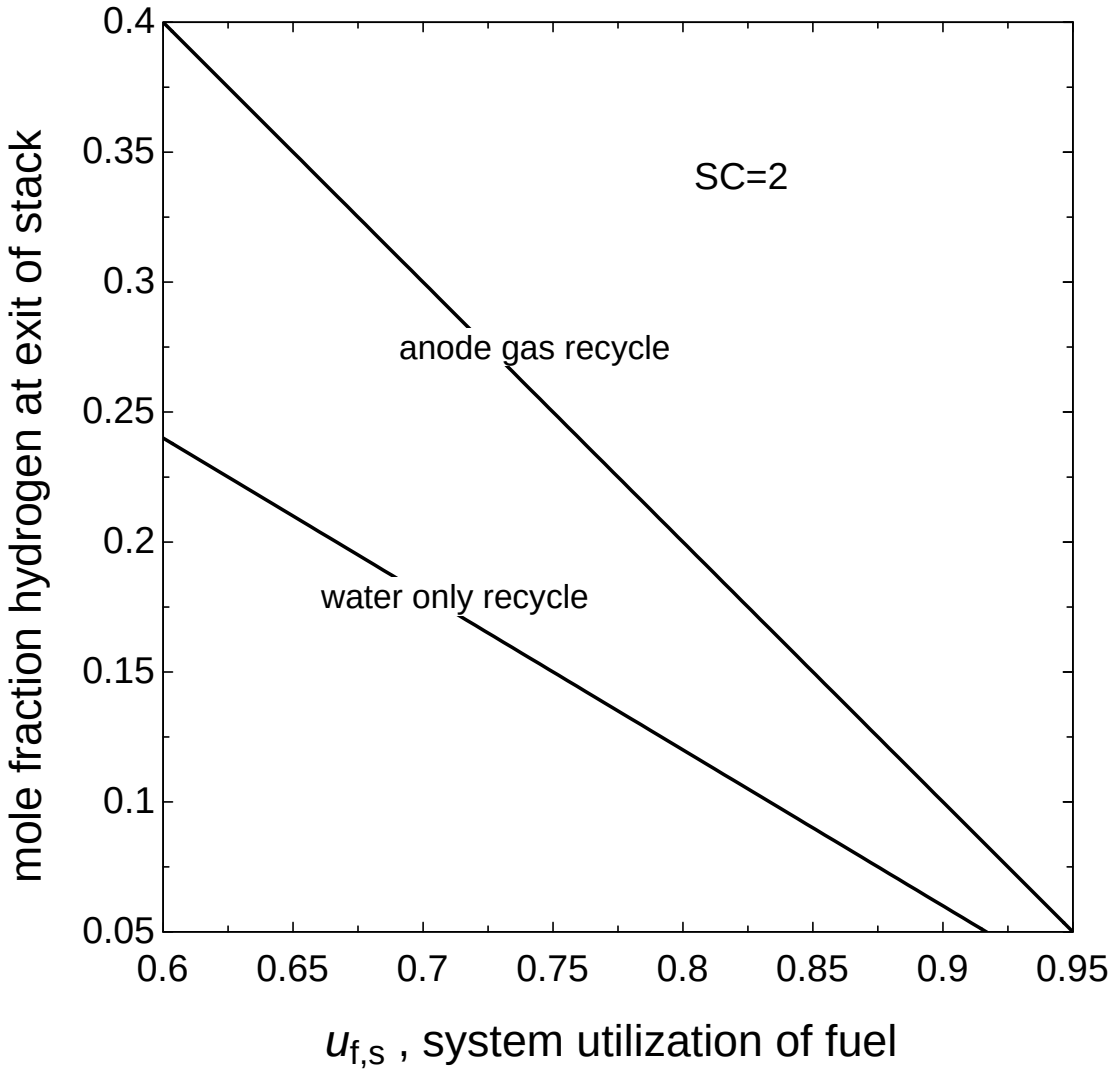

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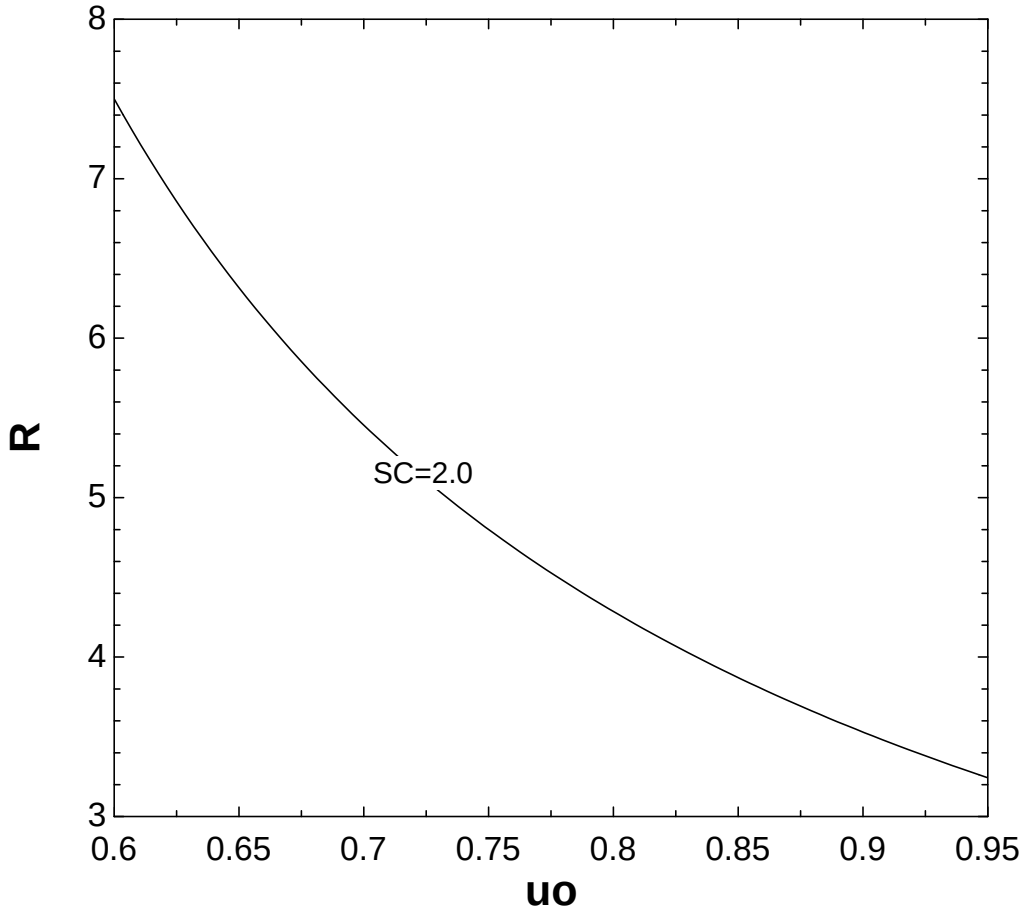

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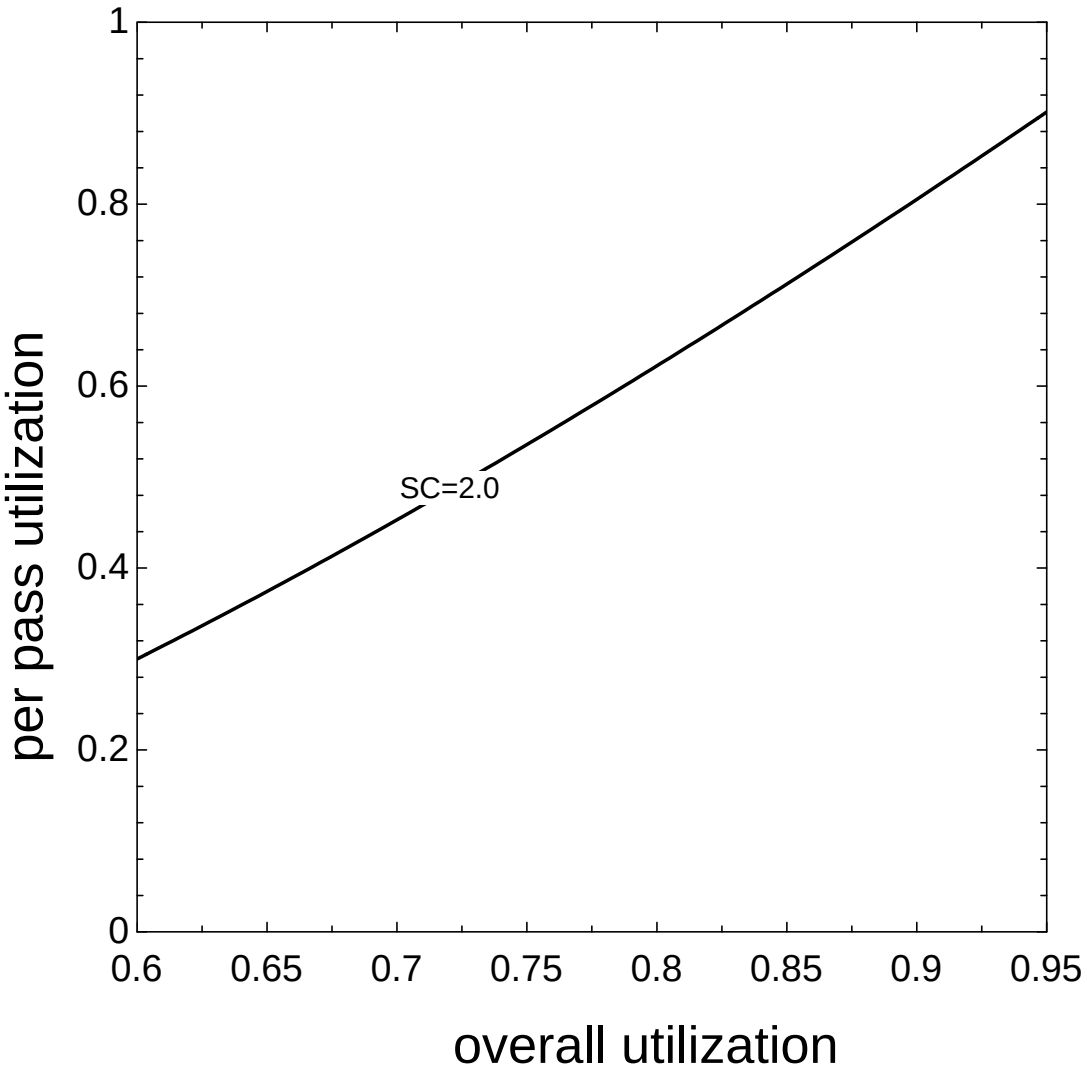

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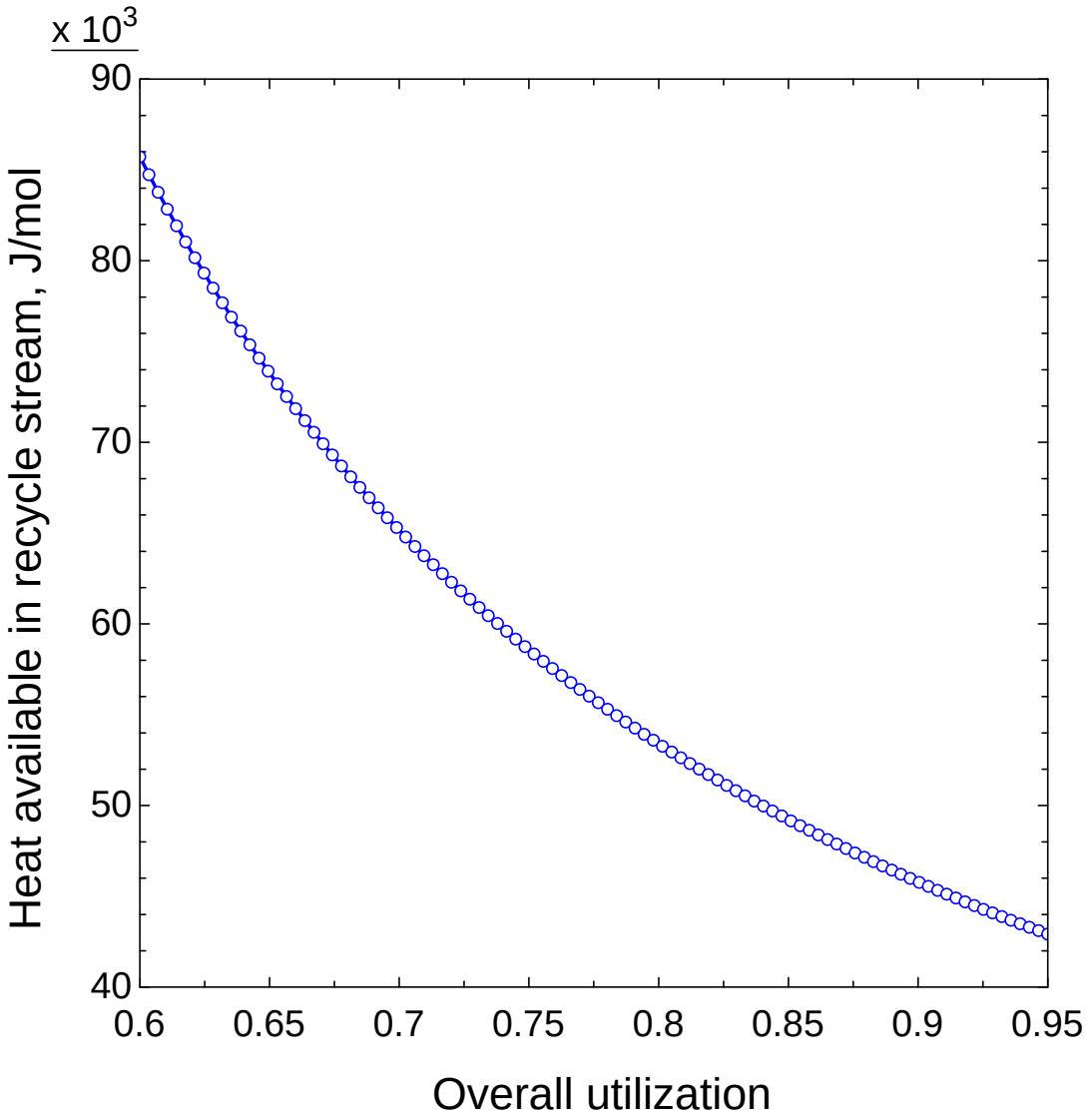

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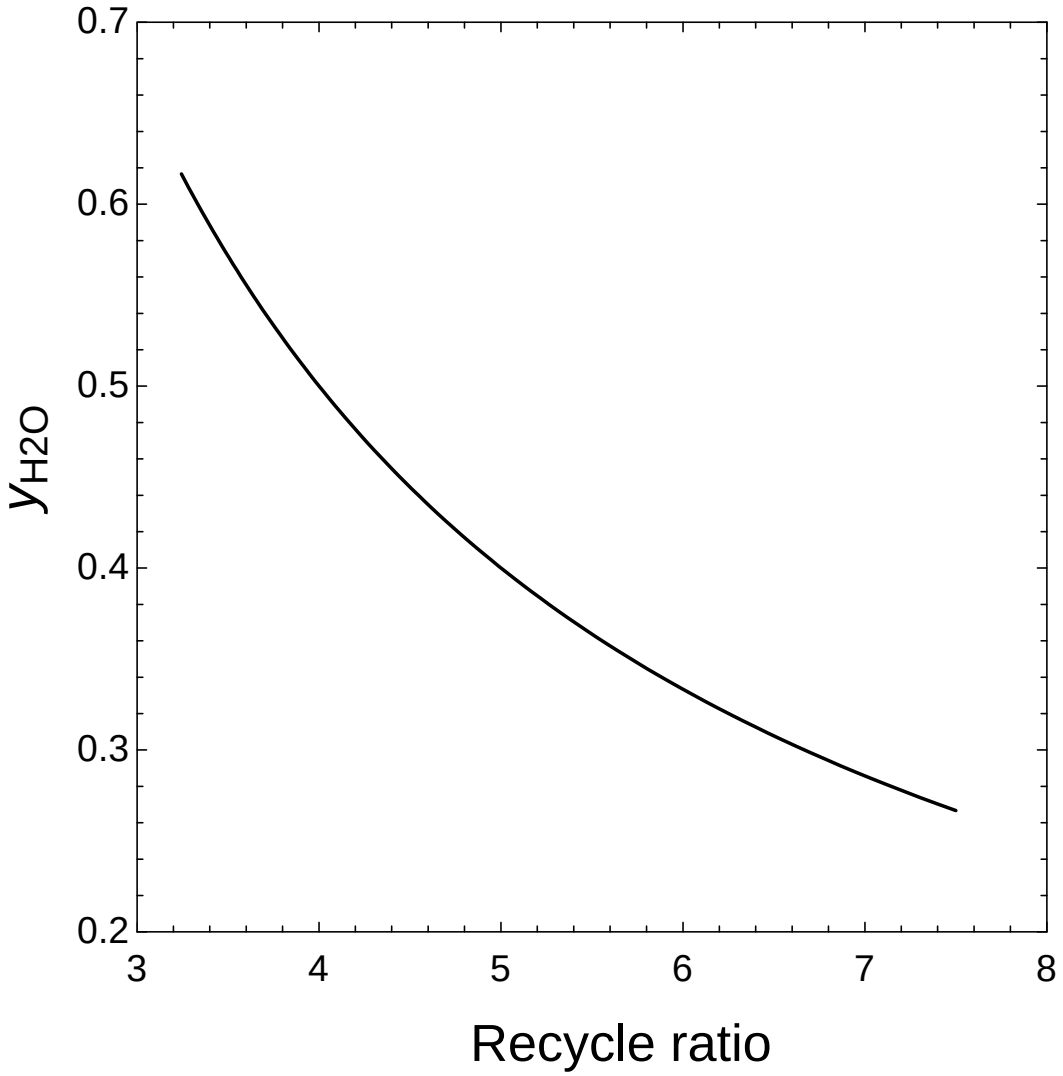

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CASE STUDY FOR SPACE FLIGHT

plf = 2 *dimensionless number that relates the mass of fuel/oxygen need to launch 1 kg of payload, baseline is 2, but doesn't affect optimization*

t = 24 · 2 · 3600 · 1 [s] *mission length in seconds, two days*

P = 2000 [W] *average conditioned power for mission duration*

ASSUMED EFFICIENCIES and oxygen utilization

η_f = 0.98 *fuel efficiency, same as hydrogen utilization*

η_{mech} = 0.9

η_{pc} = 0.95

u_o = 0.95 *oxygen utilization*

stack details

$\frac{1}{pitch}$ = 0.004 [m] *thickness of cells*

Ar = 0.7 *active area to cell area*

ρ = 2000 [kg/m^3] *estimate of stack density*

mf = 2 *total system mass divided by stack mass, baseline is 2.0*

$$m_{fcs} = \frac{A}{Ar \cdot pitch} \cdot \rho \cdot mf$$

TO START ASSUME A VOLTAGE AND CURRENT DENSIT OF CELL

$$V_{cell} = 1.15\ [V] - I_{cell} \cdot R_{OHM} - 0.07\ [V] \cdot \mathbf{log}\left[\frac{I_{cell}}{I_{ref}}\right] + V_{mt}$$

$$V_{mt} = 0.07\ [V] \cdot \mathbf{log}\left[1 - \frac{I_{cell}}{I_{mt}}\right]$$

R_{OHM} = 0.000008 [Ω-m^2]

I_{ref} = 3 [A/m^2]

I_{mt} = 16000 [A/m^2]

I_{cell}=6000 [A/m^2]

eta_{vt}=0.9

*eta_{th}=eta_f*eta_{vt}*eta_{pc}*eta_{mech}*

hydrogen and oxygen consumption for fuel cell operation

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$$m_h = \frac{P}{V_{cell}} \cdot t \cdot \frac{MW_h}{\eta_{mech} \cdot \eta_f \cdot \eta_{pc} \cdot n_a \cdot F}$$

$$m_o = 0.5 \cdot m_h \cdot \frac{\eta_f}{u_o} \cdot \frac{MW_o}{MW_h}$$

cell area

$$P_g = \frac{P}{\eta_{pc} \cdot \eta_{mech}}$$

$$P_g = I_{cell} \cdot V_{cell} \cdot A$$

CONSTANTS

$F = 96485$ [Coulomb/mol]

$n_a = 2$ *electrons transferred in hydrogen oxidation*

$MW_h = 0.002$ [kg/mol]

$MW_o = 0.016$ [kg/mol]

total mass of fuel and oxidant used

$$m_{tot} = m_{fcs} + m_h + m_o$$

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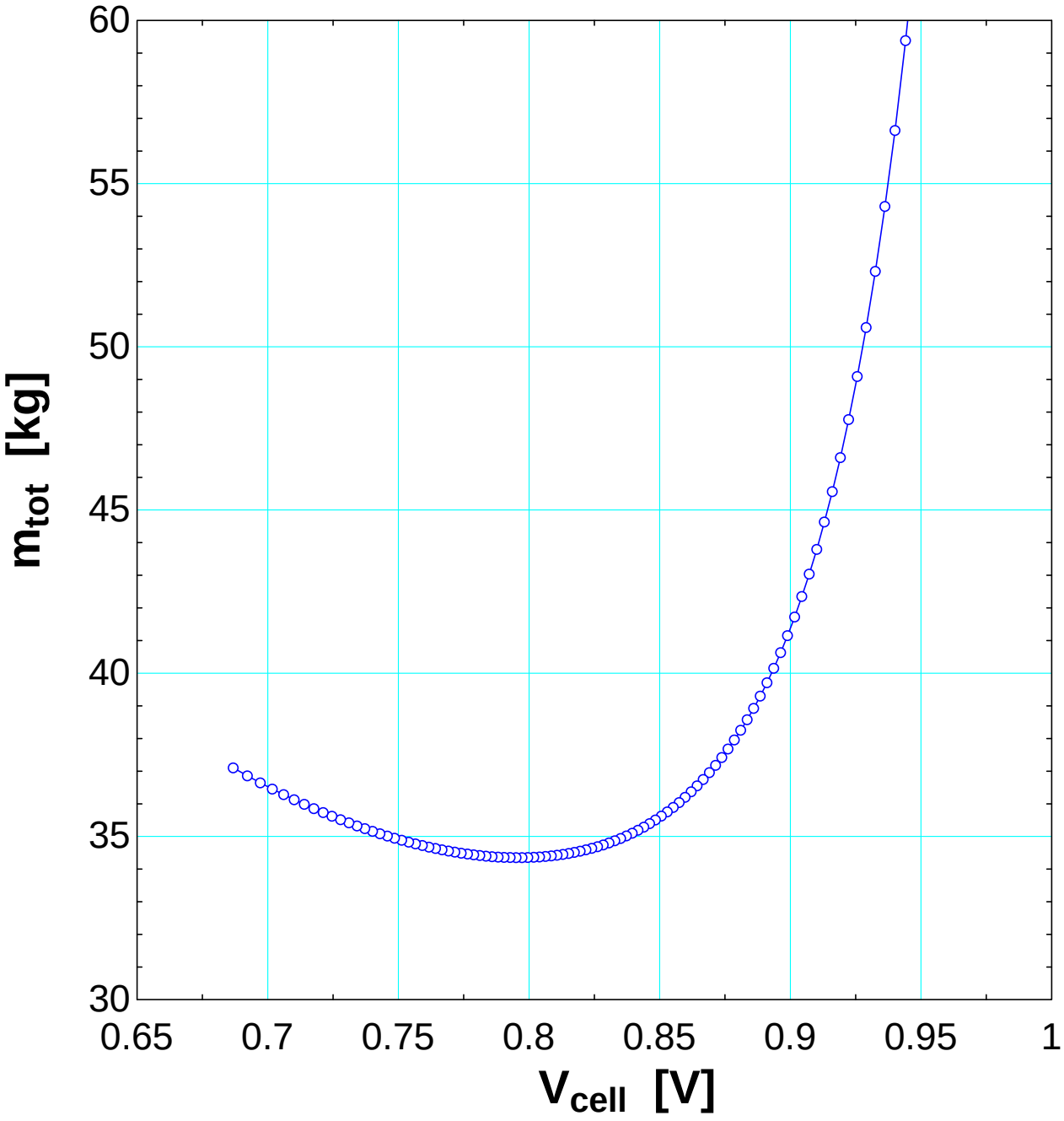


Methanol can be oxidized in an aqueous fuel cell to carbon dioxide and water as per the following cell reaction:

$$CH_3OH(\ell) + 3/2\ O_2 \rightarrow CO_2 + 2H_2O(\ell)$$

a. Write the individual electrode reactions for the fuel cell.

b. Calculate the theoretical specific energy for the fuel and report it in W·h kg^{-1}.

c. Calculate the maximum thermal efficiency for this reaction at 298 K.

d. If such a methanol cell were operating at 298 K at 0.5 V and 0.1 A, calculate the voltage efficiency and the rate of heat output from the cell.

For an acid cell, the two half-cell reactions are

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O_{(\ell)}$$

$$CH_3OH + H_2O_{(\ell)} \rightarrow CO_2 + 6H^+ + 6e^-$$

and the overall reaction is

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O_{(\ell)}$$

b) Use data from Appendix C

$$\Delta G^o_{Rx} = 2\Delta G^o_{f,H_2O} + \Delta G^o_{f,CO_2} - \Delta G^o_{f,CH_3OH}$$

$$\Delta G^o_{Rx} = 2(-327.129) + (-394.359) - (-166.6) = 702\ \text{kJ mol}^{-1}$$

$$\frac{702{,}017\ \text{J}}{\text{mol}}\left|\frac{\text{W}\cdot\text{h}}{3600\ \text{J}}\right|\frac{\text{mol}}{0.042\ \text{kg}} = 4.64\ \text{kW}\cdot\text{h kg}^{-1}$$

c) use Equation 10.4

$$\eta_{th} = \left(\frac{\Delta G}{\Delta H}\right)$$

$$\Delta H^o_{Rx} = 2(-285.830) + (-393.509) - (-239.2) = 725.97\ \text{kJ mol}^{-1}$$

$$\eta_{th} = \left(\frac{\Delta G}{\Delta H}\right) = \frac{702.017}{725.97} = 0.97$$

d) V=0.5 V

$$\eta_{th} = \frac{V}{U}\left(\frac{\Delta G}{\Delta H}\right) = \frac{0.5}{1.21}(0.97) = 0.4$$

60 percent of the energy of the fuel goes to heat.

In illustration 11-1 the specific capacitance of carbon was calculated to be 150 F/g. To fabricate an electrochemical double layer capacitor, even if the separator, current collector, and packaging weights are ignored, the theoretical value for capacitance in F/g must be reduced by a factor of exactly four. Why?

To make a device, two electrodes are needed. That doubles the mass. Also these two electrodes are effectively two capacitors in series. From Equation 11.7

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \cdots + \frac{1}{C_n}. \tag{11-7}$$

For two capacitors of equal size

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_1} = \frac{2}{C_1}.$$

or

$$C = \frac{C_1}{2}$$

this represents another factor of two reduction

$$\frac{150}{4} = 37.5 \text{ F g}^{-1}$$

Derive equation 11-8 for a 1:1 electrolyte. Hint, start with Poisson's equation (2-35) and follow the development in section 2-13. Hint: use Cartesian coordinates and do not make the assumption of a small potential. Finally, the following transform is helpful.

$$\frac{1}{2}\frac{d}{d\phi}\left(\frac{d\phi}{dx}\right)^2 = \frac{d^2\phi}{dx^2}$$

$$\nabla^2\phi = \frac{-\rho_e}{\varepsilon} = \frac{-F}{\varepsilon}\sum_i z_i c_i \ . \qquad (2\text{-}35)$$

For 1-D, Cartesian coordinates

$$\frac{d^2\phi}{dx^2} = \frac{-\rho_e(x)}{\varepsilon}$$

Assume the distribution is given by the Boltzmann factor

$$\frac{d^2\phi}{dx^2} = \frac{-F}{\varepsilon}\sum_i z_i c_i^\infty \exp\left\{\frac{-z_i F\phi}{RT}\right\}$$

Use the transform provide in the problem statement

$$\frac{1}{2}\frac{d}{d\phi}\left(\frac{d\phi}{dx}\right)^2 = \frac{-F}{\varepsilon}\sum_i z_i c_i^\infty \exp\left\{\frac{-z_i F\phi}{RT}\right\}$$

integrate using $x \to \infty$ $\phi \to 0$ and $\frac{d\phi}{dx} \to 0$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2RT}{\varepsilon}\sum_i c_i^\infty \left[\exp\left\{\frac{-z_i F\phi}{RT}\right\} - 1\right]$$

For a symmetric electrolyte (1:1 or 2:2)

$$|z_+| = |z_-| \equiv z$$

$$c_+ = c_- \equiv c$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2RTc^\infty}{\varepsilon}\left[\exp\left\{\frac{-zF\phi}{RT}\right\} - 1 + \exp\left\{\frac{zF\phi}{RT}\right\} - 1\right]$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2RTc^\infty}{\varepsilon}\left[\exp\left\{\frac{-zF\phi}{RT}\right\} + \exp\left\{\frac{zF\phi}{RT}\right\} - 2\right]$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2RTc^\infty}{\varepsilon}\left[\exp\left\{\frac{-zF\phi}{2RT}\right\} - \exp\left\{\frac{zF\phi}{2RT}\right\}\right]^2$$

Use the definition

$$\sinh u = \frac{e^u - e^{-u}}{2}$$

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{8RTc^\infty}{\varepsilon}\sinh^2\left\{\frac{zF\phi}{2RT}\right\}$$

Apply Gauss's law

$$Q = \sigma A = \iint \varepsilon E \cdot dS = -\varepsilon \left.\frac{d\phi}{dx}\right|_{x=0}$$

$$Q = -\varepsilon\sqrt{\frac{8RTc^\infty}{\varepsilon}}\sinh\frac{zF\phi}{2RT}$$

This represents the charge in the electrolyte—the charge on the metal is the opposite

$$C_{GC} = \frac{dQ_m}{d\phi} = \frac{zF}{2RT}\varepsilon\sqrt{\frac{8RTc^\infty}{\varepsilon}}\cosh\frac{zF\phi}{2RT}$$

$$C_{GC} = \varepsilon\sqrt{\frac{2z^2F^2c^\infty}{RT\varepsilon}}\cosh\left(\frac{zF\phi}{2RT}\right)$$

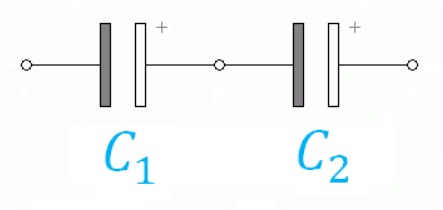
Using the definition for the Debye length, l, and introducing relative permittivity

$$C_{GC} = \frac{\varepsilon_r\varepsilon_o}{\lambda}\cosh\left\{\frac{zF\phi}{2RT}\right\}$$

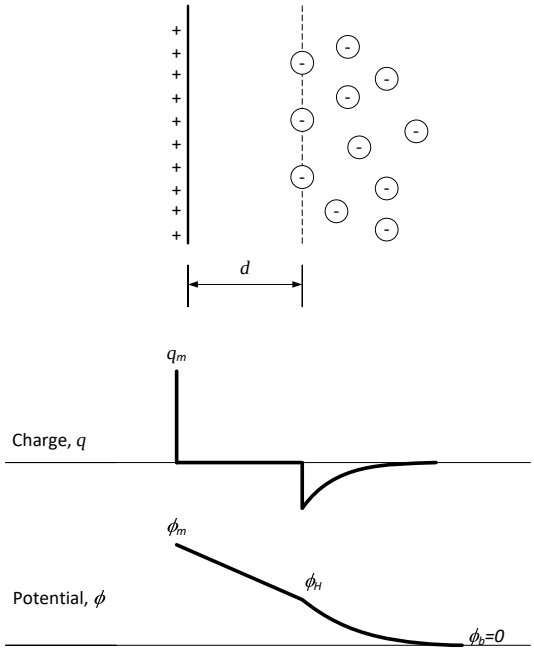
Problem 11.3

During formation, under anodic conditions Al and Ta form a thin oxide layer that serves as the dielectric separator. These materials have a rectifying property and reversing the polarity results in high current flow. Oxidation of the aluminum foil of what is normally the cathode occurs; simultaneously, the dielectric layer on the anode dissolves and hydrogen gas is released as water is reduced. The ~1.5 V tracks with the electrolysis of water.

If two, same-value electrolytic capacitors are connected in series with the positive terminals or the negative terminals connected together, the resulting single capacitor is a non-polar capacitor equal in capacitance to half of the rated capacitance of either of the original pair.



Sketch the charge density and potential across a double layer that includes both charge in the compact layer near the electrode (OHP) and the diffuse layer (GC). Assume the metal is positively charged. Develop equation 11-9 showing that the two capacitances combine in series



For 1-D, Cartesian coordinates, Poisson's equation is

$$\frac{d^2\phi}{dx^2} = \frac{-\rho_e(x)}{\varepsilon}$$

For the OHP, between the electrode and d, there is no charge; therefore the potential changes linearly.

$$\frac{d^2\phi}{dx^2} = 0$$

$$\phi(x) = Ax + B$$

In the diffuse layer, Assume the distribution of charge is given by the Boltzmann factor

$$\frac{d^2\phi}{dx^2} = \frac{-F}{\varepsilon}\sum_i z_i c_i^{\infty} \exp\left\{\frac{-z_i F\phi}{RT}\right\}$$

Assume a small potential,

$$\frac{d^2\phi}{dx^2} \approx \frac{-F}{\varepsilon}\sum_i z_i c_i^{\infty}\left(1 - \frac{z_i F\phi}{RT}\right)$$

Electroneutrality in the bulk requires that $\sum_i z_i c_i^{\infty} = 0$

$$\frac{d^2\phi}{dx^2} - \beta^2\phi = 0$$

where β is a constant.

$$\phi = A\exp\{-\beta x\} + B\exp\{\beta x\}$$

Since far from the surface the potential is zero, B=0

$$\phi = A\exp\{-\beta x\}$$

Exponential decay in the diffuse layer.

Based on the image above

$$\frac{1}{C} = \frac{d(\phi_m - \phi_b)}{dq_m}$$

$$\phi_m - \phi_b = (\phi_m - \phi_H) - (\phi_H - \phi_b)$$

so

$$\frac{1}{C} = \frac{d(\phi_m - \phi_H)}{dq_m} + \frac{d(\phi_H - \phi_b)}{dq_D}$$

where we have made use of the fact that the charge in the diffuse layer is the negative of q_m. Next apply Gauss's law

$$q = -\varepsilon\frac{d\phi}{dx}$$

Outside the Helmholtz plane, the gradient in potential is a constant, $\frac{d\phi}{dx} = \frac{\phi_m - \phi_H}{d}$

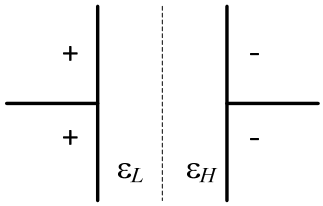
$$\frac{1}{C_{OHP}} = \frac{d}{\varepsilon} = \frac{d(\phi_m - \phi_b)}{dq_m}$$

In the diffuse layer,

$$\frac{1}{C_{GC}} = \frac{d(\phi_H - \phi_m)}{dq_m} = \frac{\lambda}{\varepsilon\cosh\frac{z_i F\phi}{2RT}}$$

$$\frac{1}{C} = \frac{1}{C_{OHP}} + \frac{1}{C_{GC}} = \frac{d}{\varepsilon} + \frac{\lambda}{\varepsilon\cosh\frac{z_i F\phi}{2RT}}$$

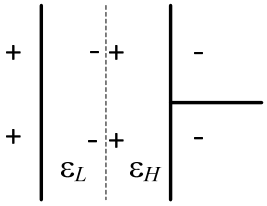
Derive equation 11-11 using the geometry of Figure 11-6. Assume that the region of low dielectric constant includes the first row of water on the electrode and a second region of high dielectric constant that extents from the ion at the OHP to the first row of water ($2r_w$).



Following the figure to the right, we can think of this situation as two capacitors in series.

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$

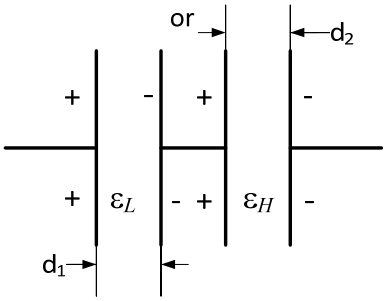
is equivalent to



where $C_1 = \frac{\varepsilon_L}{d_1}$ and $C_2 = \frac{\varepsilon_H}{d_2}$

Apply to Figure 11.6,

$$\frac{1}{C_{OHP}} = \frac{2r_w}{\varepsilon_L} + \frac{r_w\sqrt{3} + r_i}{\varepsilon_H}$$



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PROBLEM 11-6

$T = 298.15$ [K]

$R = 8.314$ [J/mol-K]

$F = 96485$ [Coulomb/mol]

$eo = 8.8542 \times 10^{-12}$ [Coulomb/(V-m)] *permittivity of free space*

PART (A) calculate Helmholtz value

$erh = 11$ *value reduced from that of water to be used in Helmholtz layer*

$\varepsilon_h = erh \cdot eo$

$$C_h = \frac{\varepsilon_h}{d}$$

$d = 4.6 \times 10^{-10}$ [m] *assumed distance, roughly molecular size of ion*

PART (B) Capacitance due to Guoy Chapman component, for 1:1 electrolyte

$erb = 78$ *bulk water value*

$\varepsilon = erb \cdot eo$

$za = -1$

$zc = 1$

$c = 50$ [mol/m^3]

$$\lambda^2 = \varepsilon \cdot R \cdot \frac{T}{F \cdot F \cdot 2 \cdot c}$$

$$C_{gc} = \frac{\varepsilon}{\lambda} \cdot \cosh\left[za \cdot F \cdot \frac{\phi}{2 \cdot R \cdot T}\right]$$

phi=0.5 [V]

estimate epsilon/lambda, should be 0.72 for 0.1 M at 25 C

PART (c)

$$\frac{1}{Cd} = \frac{1}{C_h} + \frac{1}{C_{gc}}$$ *capacitors in series*

PART (D)

Because the capacitances are in series, the smaller value controls the total capacitance, equation 11-7. Other than near the pzc, the capacitance is essentiall than given by the Helmholtz value, which is directly proportional to the dielectric constant. Therefore, having an accurate value for this parameter is critical

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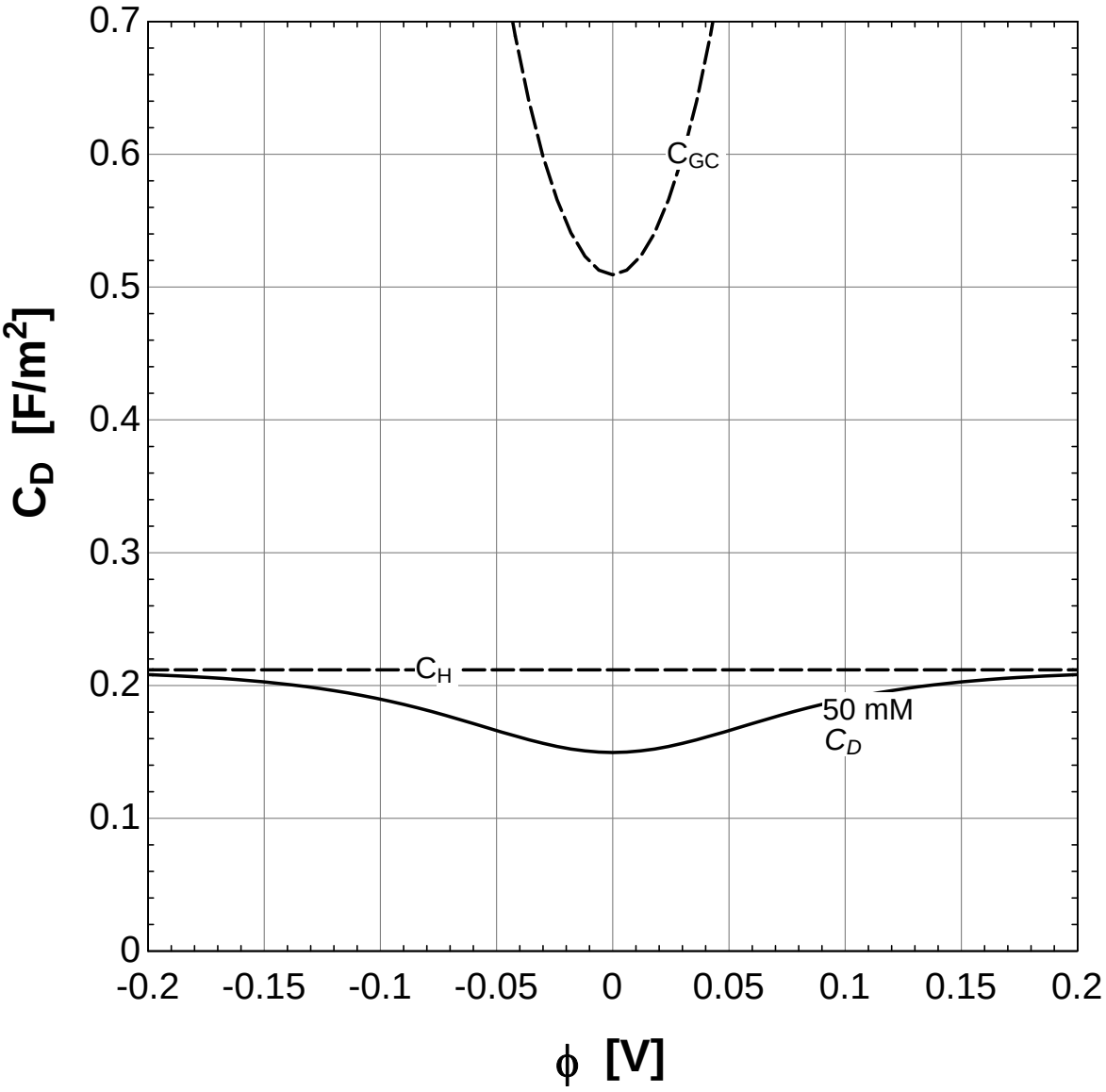

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PROBLEM 11-7a

$T = 298.15$ [K]

$R = 8.314$ [J/mol-K]

$F = 96485$ [Coulomb/mol]

$eo = 8.8542 \times 10^{-12}$ [Coulomb/(V-m)] *permittivity of free space*

PART A

Capacitance due to Guoy Chapman component, for 1:1 electrolyte

$erb = 78$ *bulk water value*

$\varepsilon = erb \cdot eo$

$za = -1$

$zc = 1$

$c = 100$ [mol/m^3] *0.1 N solution*

$$\lambda^2 = \varepsilon \cdot R \cdot \frac{T}{F \cdot F \cdot 2 \cdot c}$$

$$C_{gc} = \frac{\varepsilon}{\lambda} \cdot \cosh\left[za \cdot F \cdot \frac{\phi}{2 \cdot R \cdot T}\right]$$

$\phi = 0$ [V] *smallest value is at the PZC*

worst case, C_{gc} is more than four times $C_{DL,}$ for this level of analysis can neglect. We can also see from figure 11-5 that at this concentration there is only a small effect of the diffuse layer

PART B

From the data, we can see that the differential capacitance is independent of the cation, therefore we can conclude that ion adsorption is not important.

PART C

calculate Helmholtz value

$erh = 40$ *value reduced from that of water to be used in Helmholtz layer*

$erL = 6$

$\varepsilon_h = erh \cdot eo$

$\varepsilon_L = erL \cdot eo$

$ri = 6.0 \times 10^{-11}$ [m]

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$rw = 1.4 \times 10^{-10}$ [m]

$$\frac{1}{C_{DL}} = 2 \cdot \frac{rw}{\varepsilon_L} + \frac{rw \cdot \sqrt{3} + ri}{\varepsilon_h}$$

calculation show here for LiCl, closely approximates experimental value. Other values are similar, indicating that the first row of water and the associated dielectric constant are important factors

SOLUTION

Unit Settings: SI C kPa kJ mass deg

c = 100 [mol/m^3]
C_{DL} = 0.1633 [coulomb/V-m^2]
C_{gc} = 0.7202 [Coulomb/V-m^2]
eo = 8.854E-12 [Coulomb/(V-m)]
ε = 6.906E-10 [Coulomb/(V-m)]
ε_h = 3.542E-10 [Coulomb/(V-m)]
ε_L = 5.313E-11 [coulomb/(V-m)]
erb = 78
erh = 40
erL = 6
F = 96485 [Coulomb/mol]
λ = 9.589E-10 [m]
ϕ = 0 [V]
R = 8.314 [J/mol-K]
ri = 6.000E-11 [m]
rw = 1.400E-10 [m]
T = 298.2 [K]
za = -1
zc = 1

No unit problems were detected.

Describe how the structure of electrode might be designed differently for aqueous and non-aqueous electrolyte.

The capacitance per unit area, C_{DL} [F m^{-2}], is about the same. The main differences are

- the voltage window of the organic solvent is likely larger (2-3 V) than that of the aqueous electrolyte (~1 V)
- the conductivity of the organic electrolyte is likely much smaller, perhaps 100 times lower, than that of the aqueous electrolyte.

assuming that we want to achieve the same energy and power from two designs, recall that

$$E = \frac{1}{2}CV^2$$

and

$$P_{max} = \frac{V^2}{4ESR_{eff}}$$

$$ESR_{eff} = ESR + 2EDR = \frac{L_s}{\kappa A} + \frac{2}{3}\frac{L_e}{\kappa A}$$

Compared to the aqueous design, the thickness of the electrode/separator must be reduced by about a factor of ten to match power.

$$\left(V_{or}/V_{aq}\right)^2 = \frac{L_{or}/\kappa_{or}}{L_{aq}/\kappa_{aq}}$$

$$(3/1)^2 = \frac{L_{or}}{L_{aq}}\left(\frac{100}{1}\right)$$

$$L_{or} \sim \frac{1}{10}L_{aq}$$

Next look at energy.

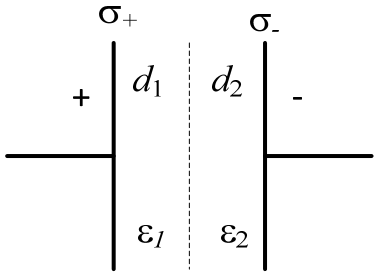
$$E = \frac{1}{2}CV^2 = \frac{1}{2}C_{DL}(La)V^2$$

Given that $\left(V_{or}/V_{aq}\right)^2 \sim 10$ and $L_{or}/L_{aq} \sim \frac{1}{10}$, the energy is roughly the same.

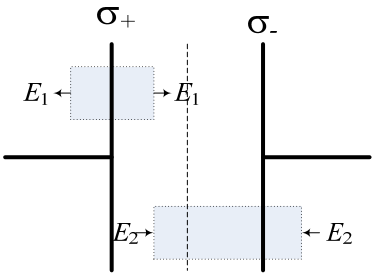
If the space between two parallel oppositely charged, infinite plates is comprised of two regions of different permittivity, how is the capacitance expressed?

Apply Gauss's law

$$\oint \varepsilon \boldsymbol{E} \cdot d\boldsymbol{S} = \int_V \rho_e \, dV$$



Apply to the two surfaces to find the electric field due to the positive charge, E_1.



$$E_1(2A) = \frac{q}{\varepsilon_1} = \frac{\sigma_+ A}{\varepsilon_1}$$

$$E_1 = \frac{\sigma_+}{2\varepsilon_1}$$

$$E_2 = \frac{-\sigma_-}{2\varepsilon_1}$$

These superpose to

$$E_{\varepsilon_1} = \frac{\sigma}{\varepsilon_1}$$

and

$$E_{\varepsilon_2} = \frac{\sigma}{\varepsilon_2}$$

The potential difference is

$$V = E_{\varepsilon_1} d_1 + E_{\varepsilon_2} d_2 = \sigma \left(\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2} \right)$$

and the capacitance per area

$$\frac{C}{A} = \frac{q}{AV} = \frac{\sigma A}{A\sigma \left(\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2} \right)}$$

or

$$\frac{1}{C} = \frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2} = \frac{1}{C_1} + \frac{1}{C_2} =$$

The same conclusion can be made from the approach of problem 11.5

The differential capacitance of a single electrode [F·m^{-2}] is fitted with this equation,

$$C_d = 0.2 + 0.1\tanh(5\phi_2).$$

Find an expression for q_m. For a practical device, two of these electrodes are used, connected in series. In operation, opposite charges of equal magnitude are stored on each electrode. Plot the differential and integral capacitance of the device as a function of potential. Comment on the degree of variation between the single electrode and the device.

$$q_m = \int_0^{\phi} C_d \, d\phi$$

$$q_m = \int_0^{\phi} 0.2 \, d\phi + \int_0^{\phi} 0.1 \tanh(5\phi) \, d\phi$$

$$q_m = 0.2\phi + 0.02 \ln[\cosh(5\phi)]$$

For the device the capacitors are in series. The charge (not potential) will be the same. The potentials are different because the capacitance is not constant.

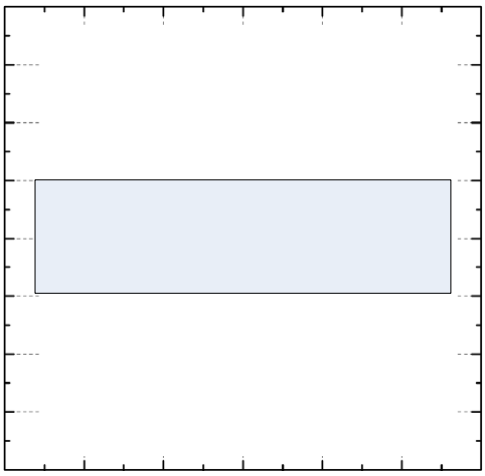
The overall capacitance is

$$\frac{1}{C} = \frac{1}{C_{d1}} + \frac{1}{C_{d2}}$$

Despite the relatively large variation in Cd for a single electrolyte with asymmetry, the combined capacitance is much more nearly constant. These results suggest that the use of a single value of the capacitance is appropriate for engineering calculations

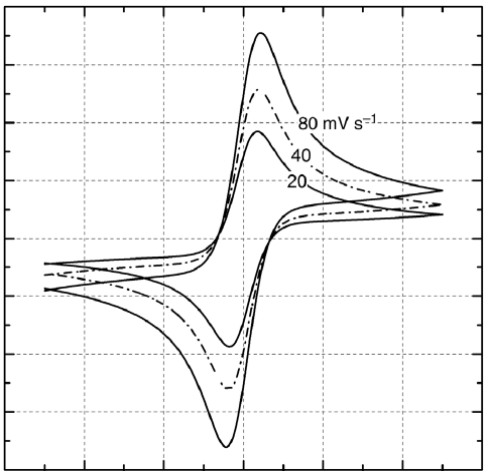
Compare and contrast differences in cyclic voltammograms for capacitors and redox reactions.

EDLC



- Rectangular
- No peaks
- Magnitude of the current proportional to scan rate

Redox reaction



- Clear peaks for oxidation and reduction
- Peak height proportional to square root of scan rate
- Mass-transfer limits current at potentials far from equilibrium

With porous electrode, often, features of both are present.

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problem 11-12

$ESR = 0.014$ [Ω]

$C = 150$ [Farad]

$Vo = 2.7$ [V]

$I = 13$ [A]

$$E = 0.5 \cdot C \cdot [Vo \cdot Vo - V \cdot V]$$

$$Qo = C \cdot Vo$$

$$Q = Qo - I \cdot t$$

$$V = \frac{Vo}{2}$$

$$Q = C \cdot V$$

$$P_{loss} = I \cdot I \cdot ESR$$

$$\eta = \frac{E - P_{loss} \cdot t}{E + P_{loss} \cdot t}$$

$$\tau = ESR \cdot C$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

C = 150 [Farad]	E = 410.1 [J]
ESR = 0.014 [Ω]	η = 0.8351
I = 13 [A]	P_{loss} = 2.366 [W]
Q = 202.5 [Coulomb]	Qo = 405 [Coulomb]
t = 15.58 [s]	τ = 2.1 [s]
V = 1.35 [V]	Vo = 2.7 [V]

No unit problems were detected.

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Problem 11-13

separator information

$L_s = 0.000025$ [m]

$k_s = 1.1$ [1/(Ω-m)]

$Area = 0.003$ [m^2]

$\rho_s = 1800$ [kg/m^3]

$\varepsilon_s = 0.5$

Electrode information

Le=50e-6 [m]

$C_s = 0.1$ [$Farad/m^2$]

$k_e = 0.7$ [1/(Ω-m)]

$ssa = 600000$ [m^2/kg] *specific surface area of carbon*

$\rho_c = 2050$ [kg/m^3]

$\varepsilon_e = 0.4$

$V = 2.3$ [V] *assumes non-aqueous electrolyte*

$\rho_e = 950$ [kg/m^3]

caculate dl capacitance

$$a = \rho_c \cdot [1 - \varepsilon_e] \cdot ssa$$

$$C_{dl} = 0.5 \cdot a \cdot L_e \cdot C_s \cdot Area$$

calculate ESR

$R_c = 0.0008$ [Ω]

$$ESR = R_c + \frac{L_s}{k_s \cdot Area}$$

calculate mass

$$m = Area \cdot [\rho_s \cdot (1 - \varepsilon_s) \cdot L_s + 2 \cdot \rho_c \cdot (1 - \varepsilon_e) \cdot L_e + \rho_e \cdot (2 \cdot \varepsilon_e \cdot L_e + L_s \cdot \varepsilon_s)]$$

kappa=80 [1/(ohm-m)]
R=Ls/kappa+L/kappa

Cv=100 [Farad/m^3]
*C=L*Cv*

L=100e-6 [m]

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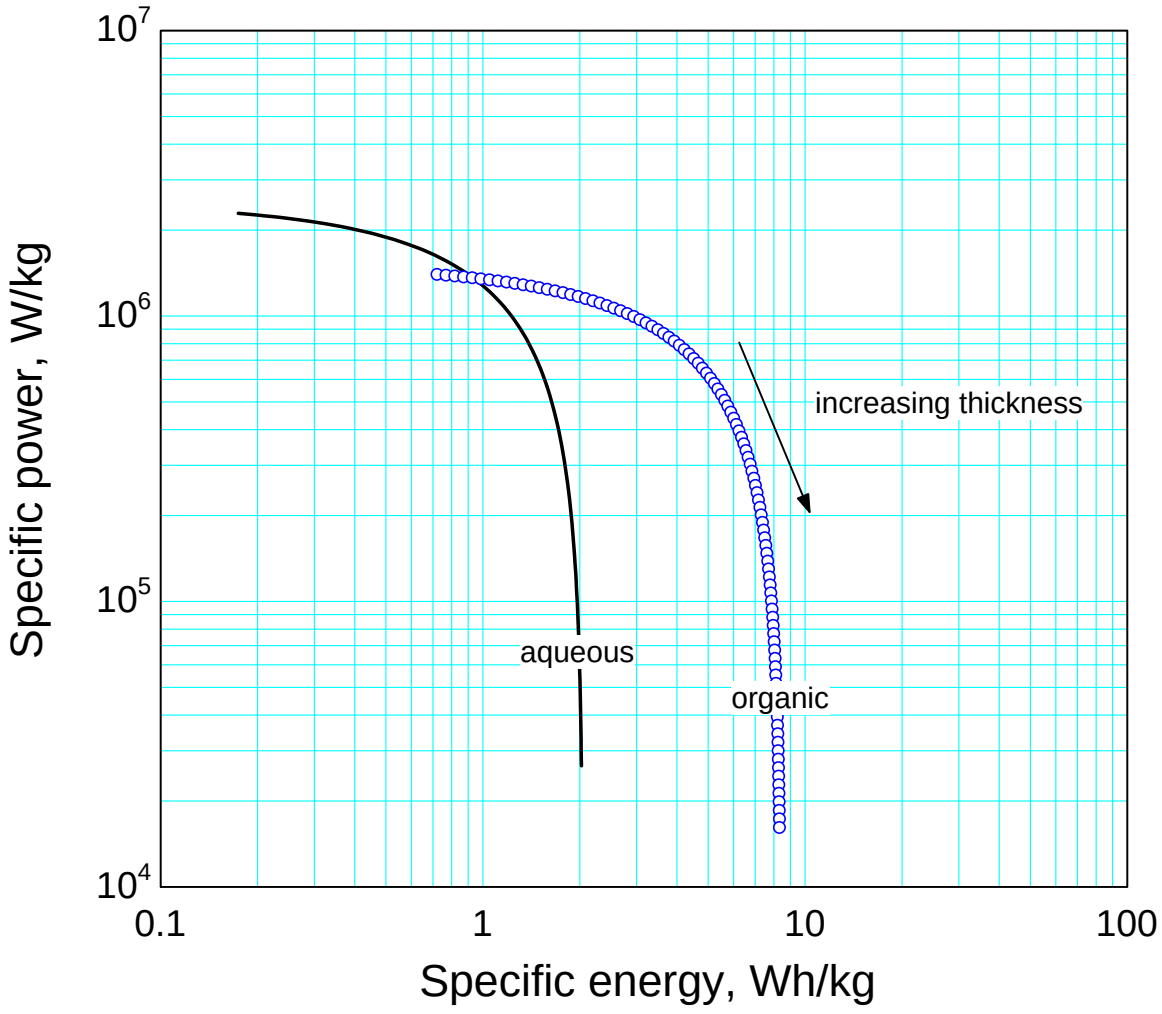
$B = 3600$ [J/W-h]

$$SE = 0.5 \cdot Cdl \cdot V \cdot \frac{V}{B \cdot m}$$

$$SP = V \cdot \frac{V}{4 \cdot ESR \cdot m}$$



A EDLC with a maximum potential of 4.2 V is charged at constant current (CC) until the potential reaches 4.2 V. The charge is then continued at 4.2 V (CV) until the current becomes very small. Finally the cell is discharge at a current of 0.1 A, starting at t=10 s. The data are shown in the figure, the inset shows the step change in current to 0.1 A for the discharge. Calculate the nominal capacitance of the EDLC and its ESR_{eff} from these data.

$$\Delta q = \int I dt = 0.1(10) = 1 \text{ C}$$

$$C = \frac{\Delta q}{\Delta V} = \frac{1}{4.2 - 1.3} = 0.35 \text{ F}$$

From the step change

$$ESR_{eff} = \frac{\Delta V}{I} = \frac{4.20 - 4.194}{0.1} = 60 \text{ m}\Omega$$

On the right are Nyquist plots for two EDLC. The only difference is the loading of the electrode, which affects the thickness and capacitance of the device. What can be said about the conductivity of the solid compared to that of the electrolyte? What are the ESR_{eff}, ESR, and EDR for the device loaded to 11.3 mg cm^{-2}? Which electrode loading would have a higher cutoff frequency? Data adapted from Taberna *et al.*, *J. Electrochem. Soc.*, **150**, A292 (2003).

a) The high frequency intercept only increases a small amount when the loading is increased. This suggest that $\sigma \gg \kappa$, but not infinite—there is a small increase

b) ESR~ 1.1 $\Omega \cdot cm^2$, the high frequency intercept.

$$ESR_{eff} = 2.4\ \Omega \cdot \text{cm}^2$$

Two identical electrodes

$$ESR_{eff} = 2(EDF) + ESR$$

$$EDF = 0.65\ \Omega \cdot \text{cm}^2$$

c) the lower loaded electrodes are thinner and since

$$\omega \propto \frac{1}{L^2}$$

the lower loaded electrodes would have a higher cutoff frequency.

In chapter seven, curves for the potential *vs.* SOC for some common insertion electrodes used in Li-ion cells were presented. Lithium titanium disulfide is an insertion material where the potential varies linearly with the concentration of lithium between the titanium disulfide galleries. Considering the discussion in section 11-8 on faradic reactions where potential changes with admitted charge, can you make the case that these insertion devices might equally well be called pseudo-capacitors?

For TiS_2,

$$V = A + Bc_s$$

where c_s is the concentration of lithium inserted in the host. The concentration is proportional to the charge transferred—it is an electron transfer reaction. Thus,

$$V = A + B'q$$

$$\frac{dV}{dq} = B' = \text{constant}$$

This defines a constant capacitance. Thus, it is reasonable to treat this as a pseudo-capacitor. This highlights that there is not always a sharp contrast between EDLCs, pseudo-capacitors, and batteries.

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PROBLEM 11-17

$\varepsilon = 0.65$

$\rho = 1800$ [kg/m^3]

$\alpha = 1$

$F = 96485$ [coulomb/mol]

c=700 [mol/m^3]

$$Qrho = \varepsilon \cdot \alpha \cdot F \cdot \left[\frac{\frac{c}{\rho}}{1 - \varepsilon} \right]$$ *equaiton 11-42*

Qrho = 50000 [coulomb/kg]

SOLUTION

Unit Settings: SI C kPa J mass deg

$\alpha = 1$
$\varepsilon = 0.65$
Qrho = 50000 [coulomb/kg]
c = 502.3 [mol/m^3]
F = 96485 [coulomb/mol]
$\rho = 1800$ [kg/m^3]

No unit problems were detected.

One mechanism for self-discharge is caused by a faradaic reaction under kinetic control, perhaps from some impurity. If the faradaic reaction is controlled by Tafel kinetics, show that the leakage current depends on the logarithm of time. Assume the capacitance is constant.

$$-i = i_o exp\left\{\frac{\alpha F}{RT}V\right\}$$

$$q = CV = C_{DL}AV$$

$$\frac{dq}{dt} = C_{DL}A\frac{dV}{dt}$$

$$-i_o exp\left\{\frac{\alpha F}{RT}V\right\}A = C_{DL}A\frac{dV}{dt}$$

$$exp\left\{\frac{-\alpha F}{RT}V\right\} = \frac{i_o}{C_{DL}}\frac{dV}{dt}$$

integrate

$$exp\left\{\frac{-\alpha F}{RT}V\right\} = \frac{\alpha F}{RT}\left\{\frac{i_o}{C_{DL}}t + A\right\}$$

where A is a constant of integration.

$$V = \frac{RT}{\alpha F}\left[\ln\left(\frac{\alpha F}{RT}\frac{i_o}{C_{DL}}\right) + \ln(t + A)\right]$$

Show that for an ideal capacitor in series with a resistance ESR, the maximum power is $V^2/4\text{ESR}$. For an ideal battery, the maximum power is $V^2/4R_{\text{cell}}$.

$$V_t = \frac{q}{C} - I(ESR)$$

and power is

$$P = IV = (V - I(ESR))I$$

maximum when derivative is zero

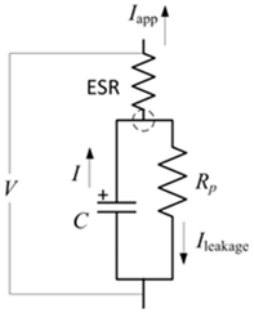
$$\frac{dP}{dI} = 2I(ESR) - V = 0$$

$$I = \frac{V}{2(ESR)}$$

$$P = \left[V - \frac{V}{2}\right]\frac{V}{2(ESR)} = \frac{V^2}{4(ESR)}$$

There are two common methods to measure leakage current. In the first, the potential of the device is measured at open-circuit over time. Explain how the $V(t)$ data can be converted to $I(t)$. Sketch how current would change over time. Why is it important to specify the time when leakage currents are reported?

Use equivalent circuit from Figure 11-19.



$$I_{leakage} = \frac{V}{R_p}$$

and

$$V = \frac{q}{C}$$

$$\frac{dV}{dt} = \frac{1}{C}\frac{dq}{dt} = \frac{-1}{C} I_{leakage}$$

at short times, V is relatively constant

$$\frac{dV}{dt} == \frac{-1}{C}\frac{V}{R_p}$$

$$\frac{dV}{V} = \frac{-1}{C}\frac{dt}{R_p}$$

$$\int_{V_i}^{V(t)} \frac{dV}{V} = -\int_0^t \frac{dt}{R_p C}$$

$$V(t) = V_i \exp\left\{\frac{-t}{R_p C}\right\}$$

The current is proportional to the potential, so that the leakage current will also decay exponentially.

Because the leakage current varies with time, it is critical to specify the time to have an accurate assessment of the severity of the leakage current.

What are some of the reasons that hybrid- and all-electric vehicles don't rely solely on regenerative braking?

a) For safety and performance, it is desired to have braking from all four wheels. To do this with regenerative braking would require that both the front and rear axles be driven electrically.
b) Friction braking is an important back-up should there be a failure in the electrical systems.
c) In the event of hard braking, the current generated may exceed the limitations of the motor/generator or inverter or the maximum C-rate that the battery may be charged.
d) The energy storage system may be fully or nearly fully charged, and therefore there is no capacity to store additional energy.

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Problem 12-2

$ts = 3$ [s]

$Vo = 16.7$ [m/s]

$m = 1600$ [kg]

t=1 [s]

$$a = \frac{-Vo}{ts}$$ *rate of acceleration required*

$V = Vo + a \cdot t$

$P = -m \cdot V \cdot a$

$Vbat = 300$ [V]

$$I = \frac{P}{Vbat}$$

$P = 40000$ [W]

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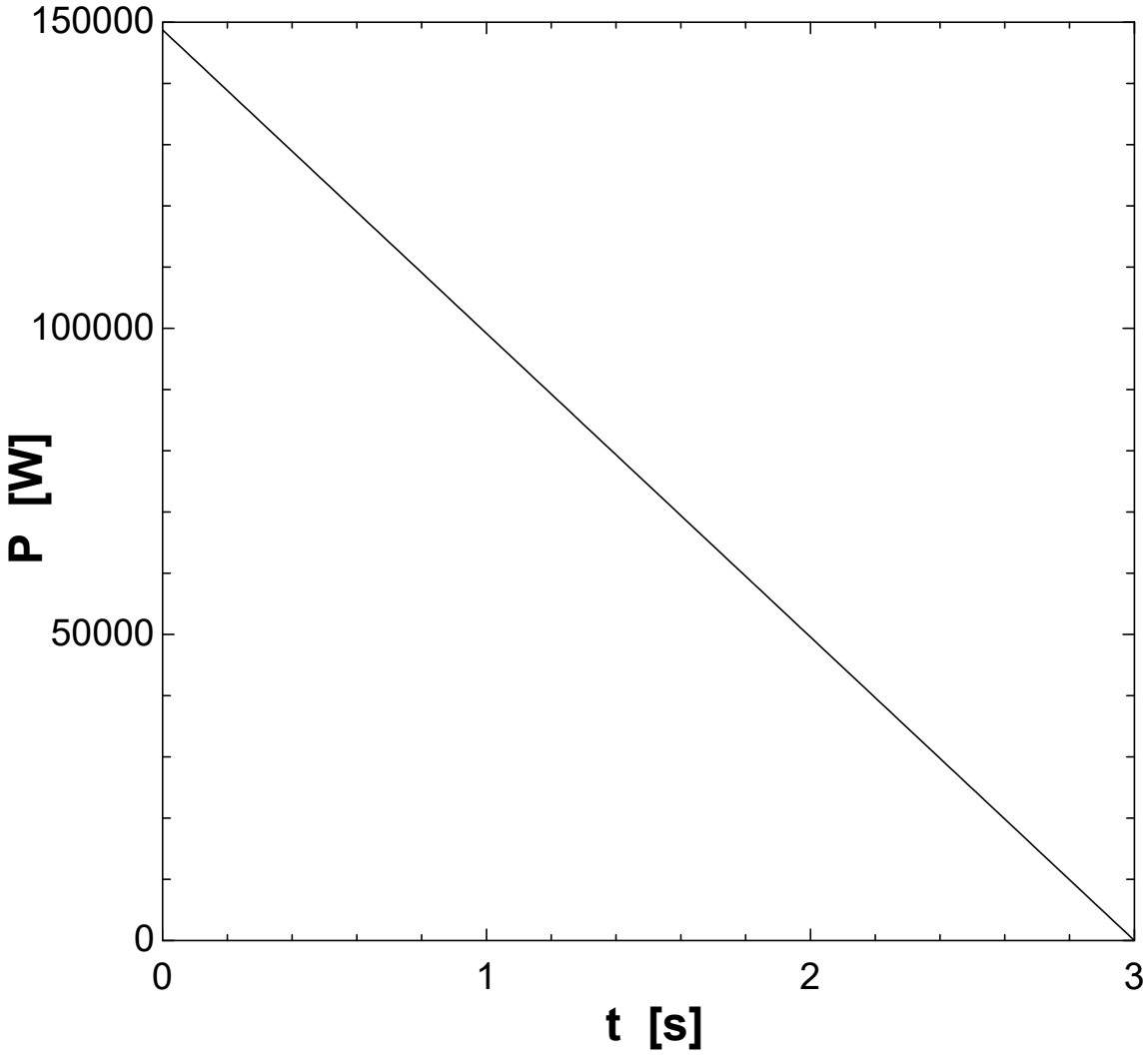

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Problem 12-3

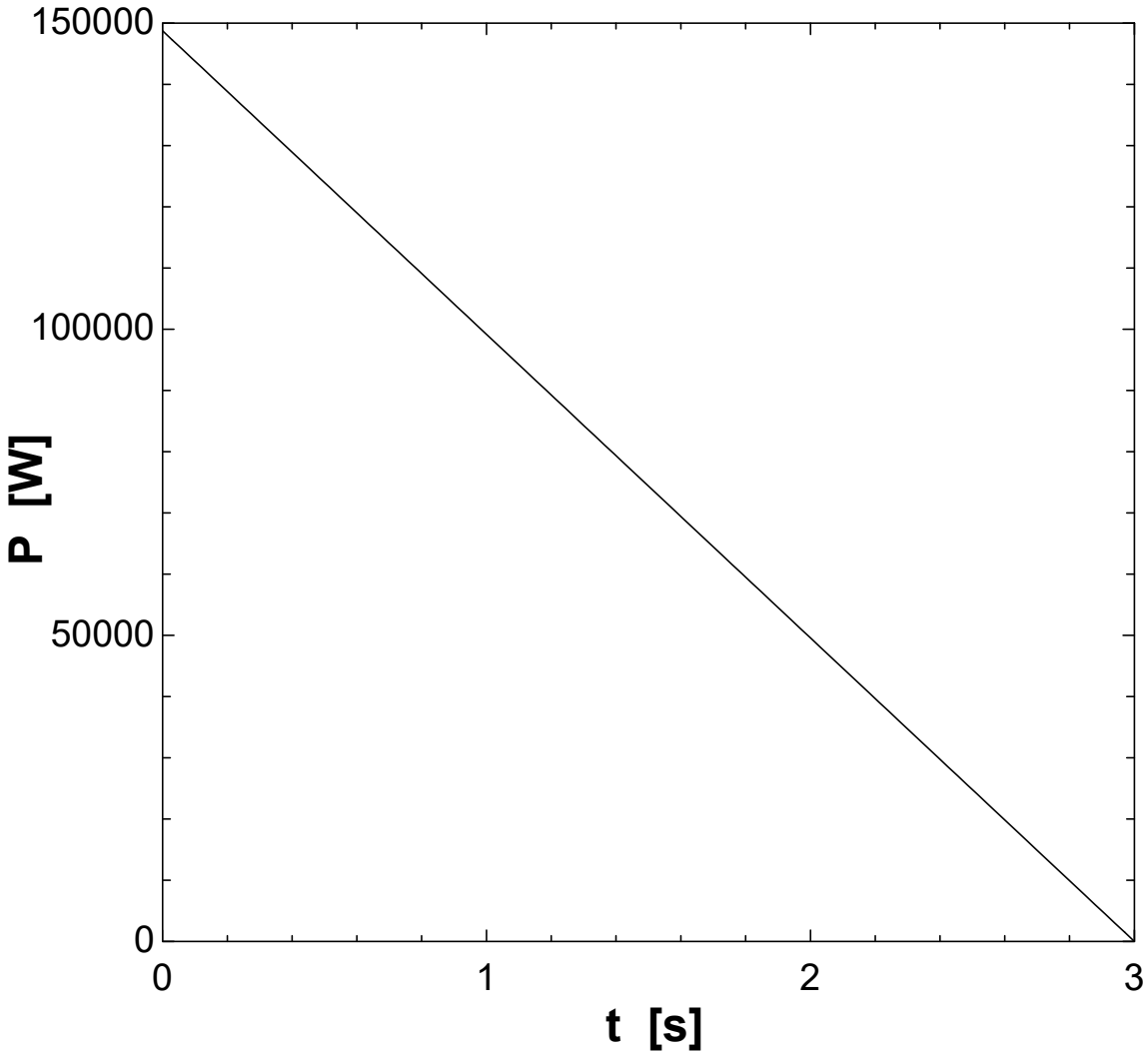
$E = 2$ [kW-h]

$cf = 3.6 \times 10^6$ [J/kW-h]

$Eb = E \cdot cf$

$m = 1750$ [kg]

$Eb = m \cdot 9.807$ [m/s^2] $\cdot$ h



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Problem 12-4

based on Honday Odyssey

$A_f = 2.8$ [m^2]

$C_d = 0.39$

v=21 [m/s]

$\rho = 1.2$ [kg/m3]

$f_r = 0.015$

$F_w = 0.5 \cdot \rho \cdot C_d \cdot A_f \cdot v \cdot v$

$F_{rd} = m \cdot 9.807$ [m/s^2] $\cdot f_r$

$P_{acc} = 400$ [W]

$P = (F_w + F_{rd}) \cdot v + P_{acc}$

$cf = 3.6 \times 10^6$ [J/kW-h]

$cf_2 = 0.001$ [km/m]

$m = 1950$ [kg]

$d = 1000$ [m]

$t = \frac{d}{v}$

$rot = cf_2 \cdot \eta \cdot d \cdot \frac{cf}{P \cdot t}$

$\eta = 1$ *efficiency of electrical energy in battery to vehicle wheels*

$rot = 6$ [km/kW-h]

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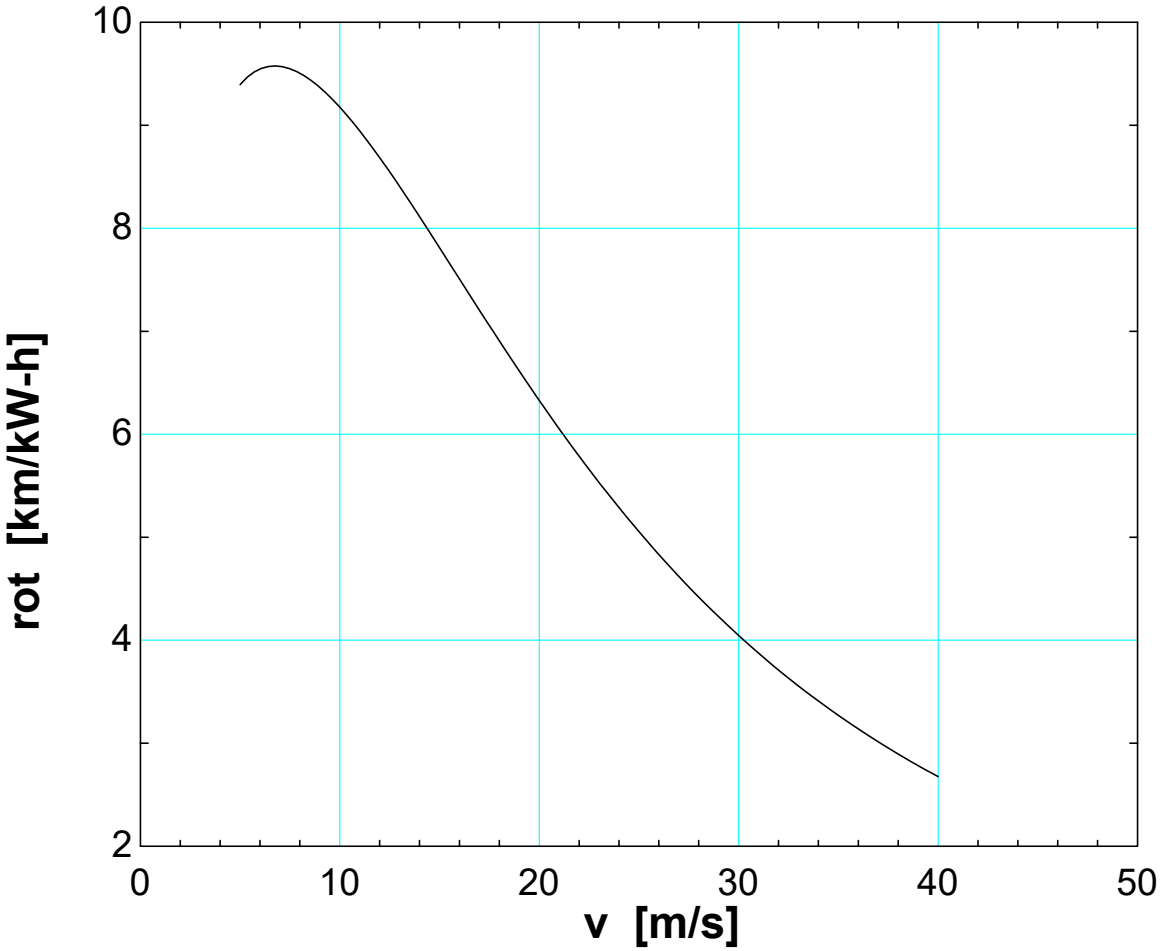

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Problem 12-5

configure battery

$d = 150$ [km]

$rot = 6$ [km/kW-h]

$E_{cb} = \frac{d}{rot}$ *energy capacity of battery*

$V_{bat} = 300$ [V]

$V_{cell} = 3.8$ [V]

$Sm = 2$ *series connected cells in module*

$Sp = 4$ *parallel connected cells in module*

$m = \textbf{Round}\left[\frac{V_{bat}}{Sm \cdot V_{cell}}\right]$ *number of modules*

$cap_c = cf1 \cdot \frac{E_{cb}}{m \cdot Sm \cdot Sp \cdot V_{cell}}$ *capacity in Ah for each cell*

$cf1 = 1000$ [W-h/kW-h]

Resistance of cells to acheive 75 kW

$P = 75000$ [W]

$V_{co} = 3.2$ [V] *cut-off potential*

$\frac{P}{m} = V_{co} \cdot \left[\frac{V_{cell} - V_{co}}{R_{mod}}\right]$ *resistance of module based on equation 12-3*

relate module resistance to cell resistance

$\frac{1}{Rs} = \frac{Sp}{R_{cell}}$

$R_{mod} = Sm \cdot Rs$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$cap_c = 21.09$ [A-h]
$d = 150$ [km]
$m = 39$
$rot = 6$ [km/kW-h]
$R_{cell} = 0.001997$ [Ω]
$Sm = 2$
$V_{bat} = 300$ [V]
$V_{co} = 3.2$ [V]
$cf1 = 1000$ [W-h/kW-h]
$E_{cb} = 25$ [kW-h]
$P = 75000$ [W]
$Rs = 0.0004992$ [Ω]
$R_{mod} = 0.0009984$ [Ω]
$Sp = 4$
$V_{cell} = 3.8$ [V]

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No unit problems were detected.

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```
"!PROBLEM 12-6"

"Battery sizing"

P=25000 [W]; "power required for power assist"

E=300 [W-h]; "energy needed"

t=E*cf1/P; "time of pulse"

cf1=3600 [J/(W-h)]
cf2=3600 [coulomb/(A-h)]

"Cell details"
R=20e-4 [ohm-m^2]; "cell resistance"
"U=3.8 [V]"
V_min=2.5 [V]
Q=12.2 [A-h/m^2]

"determine change in SOC for pulse power"

P_A=V_min*(U-V_min)/R
Q_v=Q*U


DELTA_soc=0.3

soc_0=0.9
soc=soc_0-DELTA_soc

DELTA_soc=E/(A*Q_v)


Uo=3.8 [V]
C=0.2 [V]
U=Uo-C*(1-soc)
```

SOLUTION

Unit Settings: SI C kPa J mass deg

$A = 22.03$ [m^2]
$C = 0.2$ [V]
$cf1 = 3600$ [J/(W-h)]
$cf2 = 3600$ [coulomb/(A-h)]
$\Delta soc = 0.3$
$E = 300$ [W-h]
$P = 25000$ [W]
$P_A = 1525$ [W/m^2]
$Q = 12.2$ [$A\text{-}h/m^2$]
$Q_v = 45.38$ [$W\text{-}h/m^2$]
$R = 0.002$ [$\Omega\text{-}m^2$]
$soc = 0.6$
$soc_0 = 0.9$
$t = 43.2$ [s]
$U = 3.72$ [V]
$Uo = 3.8$ [V]
$V_{min} = 2.5$ [V]

No unit problems were detected.

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Describe the main differences between series and parallel hybrid drive trains. Typically, series drive trains have larger batteries and smaller engines compared to parallel architectures, why? Which would be preferred in city stop-and-go driving? highway driving?

a) In a series hybrid, all propulsion power goes through an electric machine; whereas with a parallel architecture, power can go through the electric machine or through the engine, which is mechanically coupled directly to the drive train.
b) Because the engine in a series hybrid does not directly power the wheels, it can operate at the lower average power levels, and the battery provides the highly variable power needed for acceleration during the driving cycles. Thus, the engine can be made smaller—of course to achieve the required total power, the battery size must be increased.
c) Series architectures are better suited to stop and go traffic. When operating under highway conditions for extended periods, power must derive from the engine regardless of the architecture. In the series architecture, mechanical energy from the engine is converted to electrical energy and then back to mechanical energy. There is an additional loss that is not present with the parallel architecture where the engine is directly coupled to the drive train.

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PROBLEM 12-8

$V1 = 50$ [km/h]

$cf1 = 3600$ [s/h]

$cf2 = 1000$ [m/km]

$V = V1 \cdot \frac{cf2}{cf1}$ *vehicle speed*

$m = 1325$ [kg] *vehicle mass*

energy

$E = 0.5 \cdot m \cdot V \cdot V$ *kinetic energy of vehicle*

Determine number of cells needed

$n = \frac{Vt}{Vc}$

$Vc = 3$ [V]

$Vt = 450$ [V]

$C = 800$ [Farad/m^2]

$E = n \cdot 3 / 8 \cdot C \cdot A \cdot Vc \cdot Vc$ *A is the total separator area, equation 12-5*

$A = n \cdot Ac$ *Ac is the separator area for a single capacitor*

SOLUTION

Unit Settings: SI C kPa kJ mass deg

A = 0.3155 [m^2]
Ac = 0.002104 [m^2]
C = 800 [Farad/m^2]
cf1 = 3600 [s/h]
cf2 = 1000 [m/km]
E = 127797 [J]
m = 1325 [kg]
n = 150
V = 13.89 [m/s]
V1 = 50 [km/h]
Vc = 3 [V]
Vt = 450 [V]

No unit problems were detected.

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PROBLEM 12-9

$C = 230$ [Farad]

$V_{max} = 15$ [V]

$Vo = 13$ [V]

$P = 5000$ [W]

$ESR = 0.003$ [Ω]

$Isd = 0.003$ [A]

$$t = C \cdot \left[\frac{Vo - \sqrt{4 \cdot P \cdot ESR}}{Isd} \right]$$

$cf = 86400$ [s/day]

$$td = \frac{t}{cf}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

C = 230 [Farad]
ESR = 0.003 [Ω]
P = 5000 [W]
td = 4.662 [day]
V_{max} = 15 [V]
cf = 86400 [s/day]
Isd = 0.003 [A]
t = 402809 [s]
Vo = 13 [V]

No unit problems were detected.

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PROBLEM 12-10

$C = 230$ [Farad]

n=2

number of modules

$V_{max} = 15$ [V]

$Vo = 8.8$ [V]

$m = 1520$ [kg]

$vs = 12.5$ [m/s] *40 km/h*

$cf1 = 3600$ [J/W-h]

kinetic energy

$KE = 0.5 \cdot m \cdot vs \cdot vs$

$$WH = \frac{KE}{cf1}$$

assume time for event, constant power

$t = 10$ [s]

$$p = \frac{KE}{t}$$ *power in*

$$I = \frac{p}{Vo}$$

$0.5 \cdot C \cdot n \cdot (V_{max}^{2} - Vo^{2}) = KE$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

C = 230 [Farad]
I = 1349 [A]
m = 1520 [kg]
p = 11875 [W]
Vo = 8.8 [V]
V_{max} = 15 [V]
cf1 = 3600 [J/W-h]
KE = 118750 [J]
n = 6.998
t = 10 [s]
vs = 12.5 [m/s]
WH = 32.99 [W-h]

No unit problems were detected.

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PROBLEM 12-11

cf1 = 3600 [J/(W-h)]

p1 = 600 [W]

t1 = 45 [s]

p2 = 5000 [W]

t2 = 0.4 [s]

Wh associated with one cycle

$$Ec = \frac{p1 \cdot t1 + p2 \cdot t2}{cf1}$$

battery details

Vb = 42 [V]

$$Qc = \frac{Ec}{Vb}$$

size for cycle life

TC = 400

$$Q = 40000 \cdot \frac{Qc}{TC}$$

specific energy

SE = 130 [W-h/kg]

$$m = Q \cdot \frac{Vb}{SE}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cf1 = 3600 [J/(W-h)]
Ec = 8.056 [W-h]
m = 6.197 [kg]
p1 = 600 [W]
p2 = 5000 [W]
Q = 19.18 [A-h]
Qc = 0.1918 [A-h]
SE = 130 [W-h/kg]
t1 = 45 [s]
t2 = 0.4 [s]
TC = 400
Vb = 42 [V]

No unit problems were detected.

Identify three advantages and three disadvantages of full-hybrid vehicles. How would improvements in energy storage technology mitigate these disadvantages?

Disadvantages of full hybrid: more components and, therefore, more expensive. The control system will be more complex, increasing cost and decreasing reliability.

Advantages: the main advantage is higher efficiency. Not only can the engine be shut-off when the vehicle is stopped and energy recovered from regenerative braking, but when the engine is operated it can be operated at a point of high efficiency. With a full hybrid, electric only propulsion is available: the amount depends on the size of the battery and the degree of hybridization.

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PROBLEM 12-13

conversion factors

$cf1 = 3.6 \times 10^6$ [J/(kW-h)]

$cf2 = 3600$ [coulomb/(A-h)]

$cf3 = 0.001$ [kW/W]

vehicle information

$range = 100$ [km]

$V_t = 300$ [V] *maximum allowable voltage of pack*

$B = 6$ [km/(kW-h)] *based on vehicle design and driving schedule*

cell information

$Vcell = 3.8$ [V]

$V_{co} = 3.1$ [V] *cutoff potential*

$CA = 31$ [A-h/m^2] *based on cell design*

$RA = 0.004$ [Ω-m^2]

size of battery

$$cap = \frac{range}{B}$$ *total capacity of battery in kW-h*

number of cells

$$Ns = \textbf{Trunc}\left[\frac{V_t}{Vcell}\right]$$ *cells in series*

$Np = 2$

Np=trunc(capa$_{c/B2}$)+1

cells in parallel

$B2 = 30$ [A-h] *maximum capacity of single cell*

$Nc = Np \cdot Ns$

$$cap_c = \frac{cap}{Nc}$$ *capacity of single cell in kW-h*

$$capa_c = \frac{cf1}{cf2} \cdot \frac{cap_c}{Vcell}$$ *capacity of single cell in Ah*

$capa_c = CA \cdot AC$ *AC is cell area*

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$$Rcell = \frac{RA}{AC} \quad \textit{cell resistance}$$

$$Pmax = cf3 \cdot Nc \cdot V_{co} \cdot \left[\frac{Vcell - V_{co}}{Rcell}\right]$$

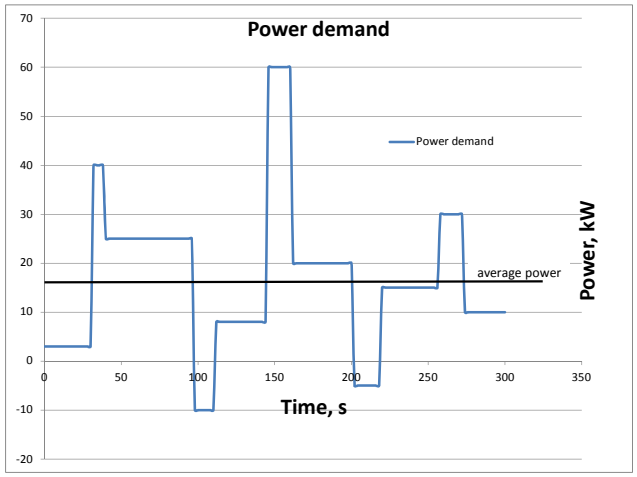
SOLUTION

Unit Settings: SI C kPa J mass deg

AC = 0.9069 [m^2]
B = 6 [km/(kW-h)]
B2 = 30 [A-h]
CA = 31 [A-h/m^2]
cap = 16.67 [kW-h]
$capa_c$ = 28.12 [A-h]
cap_c = 0.1068 [kW-h]
cf1 = 3.600E+06 [J/(kW-h)]
cf2 = 3600 [coulomb/(A-h)]
cf3 = 0.001 [kW/W]
Nc = 156
Np = 2
Ns = 78
Pmax = 76.75 [kW]
RA = 0.004 [Ω-m^2]
range = 100 [km]
Rcell = 0.00441 [Ω]
Vcell = 3.8 [V]
V_{co} = 3.1 [V]
V_t = 300 [V]

No unit problems were detected.

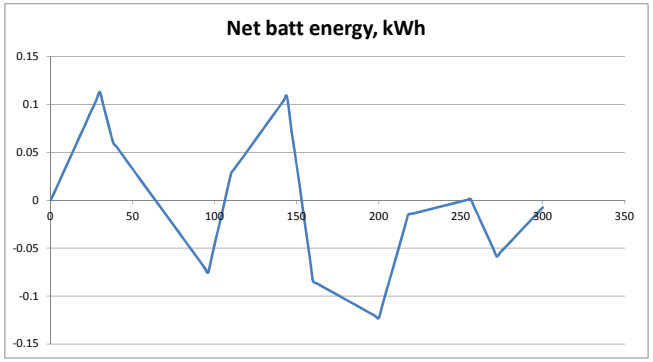
time	power	Battery power	Net batt energy
0	3	-13.5497	0
2	3	-13.5497	0.007528
4	3	-13.5497	0.015055
6	3	-13.5497	0.022583
8	3	-13.5497	0.03011
10	3	-13.5497	0.037638
12	3	-13.5497	0.045166
14	3	-13.5497	0.052693
16	3	-13.5497	0.060221
18	3	-13.5497	0.067748
20	3	-13.5497	0.075276
22	3	-13.5497	0.082804
24	3	-13.5497	0.090331
26	3	-13.5497	0.097859
28	3	-13.5497	0.105386
30	3	-13.5497	0.112914
32	40	23.45033	0.099886
34	40	23.45033	0.086858
36	40	23.45033	0.07383
38	40	23.45033	0.060802
40	25	8.450331	0.056107
42	25	8.450331	0.051413
44	25	8.450331	0.046718
46	25	8.450331	0.042024
48	25	8.450331	0.037329
50	25	8.450331	0.032634
52	25	8.450331	0.02794
54	25	8.450331	0.023245
56	25	8.450331	0.01855
58	25	8.450331	0.013856
60	25	8.450331	0.009161
62	25	8.450331	0.004467
64	25	8.450331	-0.00023
66	25	8.450331	-0.00492
68	25	8.450331	-0.00962
70	25	8.450331	-0.01431
72	25	8.450331	-0.01901
74	25	8.450331	-0.0237
76	25	8.450331	-0.0284



avg power	16.55 kW				
max	60				
min	-10				
FC power	16.5 kW			DOH	0.344301
Batt power	43.5 kW	max C discharge	5	DOH	0.23402
Batt P min	-26.5	max C charge	2		
Batt energy kWh	0.236	Bat kWh	8.7	Bat kWh	13.3
		ΔSOC	2.7	ΔSOC	1.8

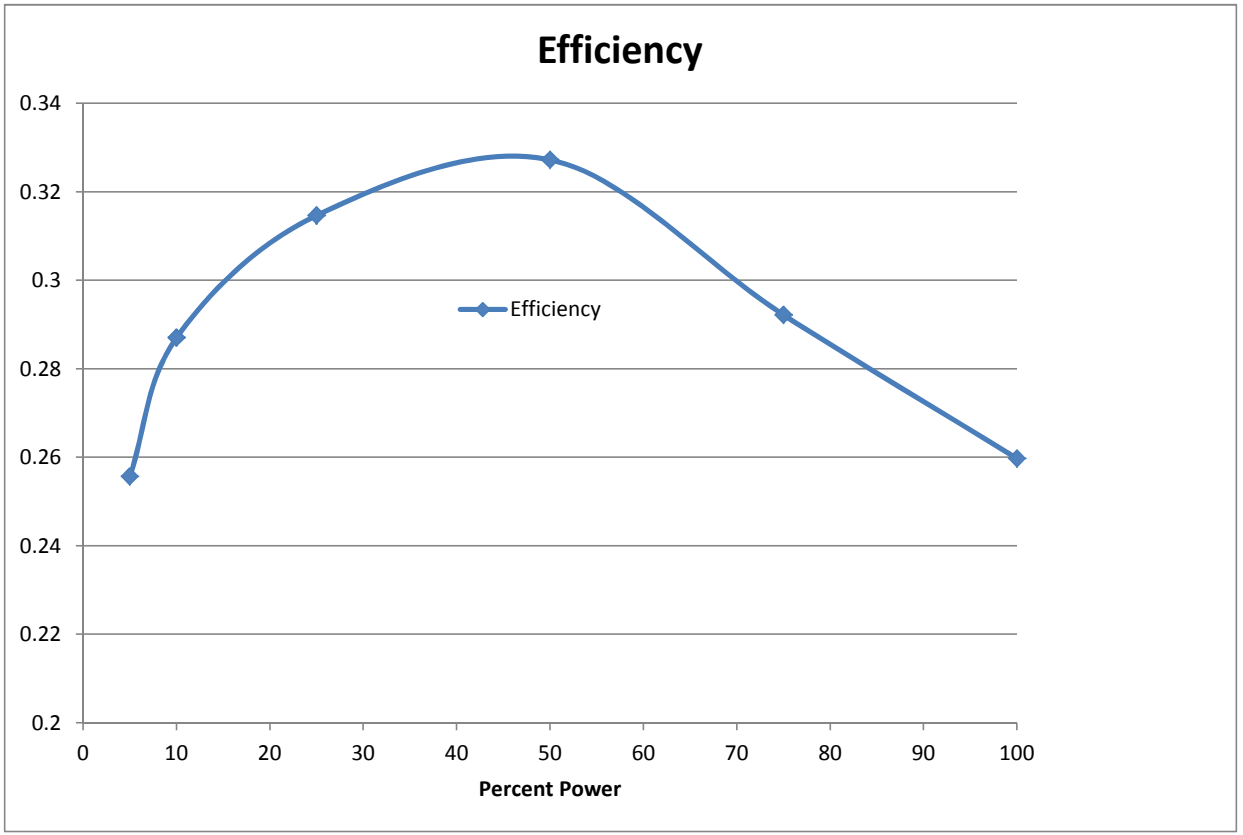
Approach

1	constant fuel cell power, sized to meet average power demand of 16.55 kW
2	battery sized to recover all excess energy without exceeding C-rate limits largest swing in energy (kWh) calculated, 0.236, cell T13 size (kWh) is calculated using max and min battery power and C-rate 13.3 kWh battery, cell z13 is needed to recover all of the energy and keep C-rate below 2
3	Note that the battery has to be quite large to recover all of the energy



power	fuel con	eff
5	320	0.255682
10	285	0.287081
25	260	0.314685
50	250	0.327273
75	280	0.292208
100	315	0.25974

The maximum efficiency is near 50 % for the ICE. This is compared to a fuel cell that has a maximum efficiency below 20 %. For the ICE hybrid it makes more sense to turn the engine off and use the battery and if the engine is used to operate at max efficiency and charge the battery with the excess power



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"!PROBLEM 12-16"

m=1700 [kg]; "vehicle mass"
vs=25 [m/s];"speed, 90 km/h=25 m/s"

"grade in percent"

tan(alpha)=6/100

vy=vs*sin(alpha)

Fy=m*g#*cos(alpha)

P=Fy*vy

SOLUTION
Unit Settings: SI C kPa kJ mass deg

α = 3.434 [degree]	Fy = 16642 [N]
m = 1700 [kg]	P = 24918 [W]
vs = 25 [m/s]	vy = 1.497 [m/s]

No unit problems were detected.

A vehicle requires 12 kW of average power, and 70 kW maximum power to complete a typical driving schedule. If 22 kW additional power is required to sustain 90 km/h up a 6 % grade, what is the maximum degree of hybridization?

$$\text{degree of hybridization} = DOH = \frac{\text{battery power}}{\text{engine power+battery power}} \quad (12\text{-}6)$$

The engine power must be sufficient to sustain speed on grade indefinitely. In this problem the engine power is 12+22 kW. The engine plus battery power is 70 kW.

$$\text{degree of hybridization} = DOH = \frac{70-12-22}{70} = 0.51 \quad (12\text{-}6)$$

Using the start-stop information from Illustration 12.3, for two EDLC modules how many attempts to start the vehicle can be made after a period of stopping for 45 s?

Restart $500W \times 0.4s = 2000J$

While stopped $600W \times 45s = 27{,}000J$

Energy in capacitor $2 \times 230FV_{max}^2 \frac{3}{8} = 38{,}813J$

$$38{,}813 = (2000)n + 27{,}000$$

$$n = 5.9$$

$$\therefore \quad 5\ attempts$$

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```
"!PROBLEM 12-19"
m=1400 [kg]
Af=0.6 [m^2]
Cd=0.5
fr=0.016

v=sp*cf
cf=(1/3.6) [h-m/s-km]
sp=90 [km/h]

Pw=0.5*Af*Cd*rho*v*v*v; "power to overcome aerodynamic drag"
rho=density(air, t=t1, p=p1)
p1=100 [kPa]
T1=20 [C]

Prd=m*g#*fr*v; "rolling resistance"

Ppar=1000 [W]

Pt=Prd+Pw+Ppar


"!rule of thumb"
t=1 [h]
cf2=1000 [m/km]
cf3=3600 [J/W-h]
cf4=1000 [W-h/kW-h]
eta=0.8
rot=eta*cf3*cf4*v/(Pt)/cf2
```

SOLUTION

Unit Settings: SI C kPa J mass deg

Af = 0.6 [m^2]	Cd = 0.5
cf = 0.2778 [h-m/s-km]	cf2 = 1000 [m/km]
cf3 = 3600 [J/W-h]	cf4 = 1000 [W-h/kW-h]
η = 0.8	fr = 0.016
m = 1400 [kg]	p1 = 100 [kPa]
Ppar = 1000 [W]	Prd = 5492 [W]
Pt = 9277 [W]	Pw = 2785 [W]
ρ = 1.188 [kg/m^3]	rot = 7.761 [km/kW-h]
sp = 90 [km/h]	t = 1 [h]
t1 = 20 [C]	v = 25 [m/s]

No unit problems were detected.

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"!PROBLEM 12-20"
m=1500 [kg]
sp=90 [km/h]
v=cf*sp

cf=(1/3.6) [h-m/s-km]

Pa=0.5*m*v*v/t
t=10 [s]

Pd=-0.5*m*v*v/td
td=4 [s]

SOLUTION
Unit Settings: SI C kPa J mass deg

cf = 0.2778 [h-m/s-km]	m = 1500 [kg]
Pa = 46875 [W]	Pd = -117188 [W]
sp = 90 [km/h]	t = 10 [s]
td = 4 [s]	v = 25 [m/s]

No unit problems were detected.

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"!PROBLEM 12-21"

Nc=80

U=3.8 [V]

Vmax=4.2 [V]

Vmax=U+I*R

P=Nc*I*Vmax; "determines current"

P=80000 [W]

Q=Nc*I*I*R; "joule heating"

SOLUTION

Unit Settings: SI C kPa J mass deg

I = 238.1 [A]	Nc = 80
P = 80000 [W]	Q = 7619 [W]
R = 0.00168 [Ω]	U = 3.8 [V]
Vmax = 4.2 [V]	

No unit problems were detected.

A large hybrid-electric transit bus is being designed. It is desired to recover the kinetic energy during stopping. The fully loaded mass is 20,000 kg, and the bus is estimated to make 200 stops per day from 50 km/h, each in 10 seconds. Using information provided below, first size a battery and then an EDLC for one year of operation, and complete the table below. The maximum allowable voltage is 600 V.

	Battery	**EDLC**
Individual cell voltage	**3.5 V (constant with SOC)**	**3.0 V (maximum)** **1.5 V (minimum)**
Specific energy	**125 Wh/kg**	**5 Wh/kg**
Energy density	**275 Wh/dm^3**	**7 Wh/dm^3**
Number of cells		
C-rate during braking		NA
Maximum current		
Capacity of RESS, kWh		
Volume of RESS		
Mass of RESS		

For the battery, the capacity turnover $= 500 + 2000(1 - \Delta_{SOC})^4$. For the EDLC, assume that the size must be increased by 20 % to meet life requirement.

	Battery	**EDLC**
Individual cell voltage	**3.5 V (constant with SOC)**	**3.0 V (maximum)** **1.5 V (minimum)**
Specific energy	**125 Wh/kg**	**5 Wh/kg**
Energy density	**275 Wh/dm^3**	**7 Wh/dm^3**
Number of cells	171	200
C-rate during braking	11	NA
Maximum current	321 A	643 A
Capacity of RESS, kWh	17.3	0.858
Volume of RESS	63 dm^3	122 dm^3
Mass of RESS	138 kg	172 kg

Corrosion protection is frequently provided by coating a steel structure with a thin coating of zinc. Please determine the time required to electroplate a 25μm layer. The density of zinc is 7.14 g/cm^3. The current density is 250 A m^{-2}, and the faradaic efficiency is 80%.

$$L = \frac{M_i \eta_c I t}{\rho A n F}$$

For zinc, $n = 2$ $\rho = 7.14\ g/cm^3$

$$M_{zn} = 0.06538 \frac{kg}{mol}$$

$$t = \frac{\rho A n F L}{M_i \eta_c I} \qquad i = \frac{I}{A}$$

$$\frac{\left(7140 \frac{kg}{m^3}\right)\left(2 \frac{equiv}{mol}\right)\left(96485 \frac{C}{equiv}\right)(25 \times 10^{-6} m)}{\left(0.06538 \frac{kg}{mol}\right)(0.8)\left(250 \frac{A}{m^2}\right)}$$

$$= 2634 s = 43.9\ minutes$$

Nickel is plated from a sulfate bath at 95 % faradaic efficiency onto a surface with a total area of 0.6 m^2. The density of nickel is 8,910 kg m^{-3}, and plating is performed at a current of 300 A. What is the thickness of the plated nickel after 30 minutes? What is the average rate of deposition?

$$L = \frac{M_i \eta_c I t}{\rho A n F}$$

$A = 0.6 m^2$

$\rho = 8.91\ g/cm^3$

$I = 300 A$

$M_{Ni} = 0.05869\ kg/mol$

$t = 30\ minutes$

$n = 2$

$$L = \frac{(0.05869)(0.95)(300)(30)(60)}{(8910)(0.6)(2)(96485)}$$

$$= 2.92 \times 10^{-5} m = 29.2 \mu m$$

$$Rate = \frac{L}{t} = \frac{29.2 \mu m}{30\ minutes} = \frac{0.97 \mu m}{minutes}$$

$$\approx \frac{1 \mu m}{minutes}$$

Electrorefining of copper involves the plating of copper onto large electrodes in tank-type cells. In one design, electrodes are plated with 5 mm of copper before they are mechanically stripped. If the electrode area is 2 m^2 and plating takes place at 200 A m^{-2} at a faradaic efficiency of 96 %, how long does it take to deposit a layer of the desired thickness? What is the mass of the plated copper? What is the total current for a production cell that contains 50 cathodes? The density of copper is 8,960 kg m^{-3}.

$L = 5mm$

$A = 2m^2$

$I = 200\ A/m^2$

$\rho_{Cu} = 8.96\ g/cm^3$

$M_{Cu} = 63.546\ g/mol$

$\eta_C = 0.96$

$$L = \frac{M_i \eta_c I t}{\rho A n F}$$

$$t = \frac{\rho A n F L}{M_i \eta_c I} \qquad i = \frac{I}{A}$$

$$= \frac{\left(8960 \frac{kg}{m^3}\right)\left(2 \frac{equiv}{mol}\right)\left(96485 \frac{C}{equiv}\right)(5 \times 10^{-3} m)}{\left(0.06355 \frac{kg}{mol}\right)(0.96)\left(200 \frac{A}{m^2}\right)}$$

$$= 708{,}520 s = 197\ hours = 8.2\ days$$

$$m_{Cu} = \rho A L = \left(8960 \frac{kg}{m^3}\right)(2m^2)(5 \times 10^{-3} m)$$

$$= 89.6\ kg\ (per\ electrode)$$

$$(50\ cathodes)\left(\frac{2m^2}{cathode}\right)\left(200 \frac{A}{m^2}\right)$$

$$= 20{,}000\ A$$

$$= 20\ kA$$

Chromium is plated from a hexavalent bath at a faradaic efficiency of about 20 %. A metal piece is to be plated to a thickness of 0.5 μm. The current density is 500 A m^{-2}.

a. How long will it take to deposit the desired amount of Cr?
b. How does the low faradaic efficiency impact the time and energy required to plate Cr?
c. There is a movement away from the use of hexavalent Cr. Why?

a. $L = 0.5\mu m$

$\eta_c = 0.20$ (Cr efficiency is low)

$I = 500\frac{A}{m^2}$ $n = 6$

Look up:

$M_{Cr} = 51.996\frac{g}{mol}$

$\rho_{Cr} = 7.19\frac{g}{cm^3}$

$$L = \frac{M_i \eta_c I t}{\rho A n F}$$

$$t = \frac{\rho A n F L}{M_i \eta_c I} \qquad i = \frac{I}{A}$$

$$= \frac{\left(7190\frac{kg}{m^3}\right)\left(6\frac{equiv}{mol}\right)\left(96485\frac{C}{equiv}\right)(5\times10^{-7}m)}{\left(0.05200\frac{kg}{mol}\right)(0.2)\left(500\frac{A}{m^2}\right)}$$

$$= 400s = 6.67\ minutes$$

b. Significant impact – lengthens time required. Only 20% of energy goes toward product.

c. Cr (VI) is a carcinogen and an environmental hazard (high toxicity)

Please determine the *B* value for a 3D cubic cluster of atoms.

$$A_s{}^3 = BV^2$$

For cube of side length L

$$A_s = 6L^2$$

$$V = L^3$$

$$(6L^2)^3 = B(L^3)^2$$

$$B = 6^3 = 216$$

Show that the perimeter, $P = 2\sqrt{\mathfrak{b}\Omega N}$ for a 2D cluster. What is Ω in this expression? Why do we need *P* as a function of *N*? How does the variation of *P* with *N* relate affect the size of the critical size of the nucleus? The critical number of atoms in a nucleus changes with overpotential. Does that mean that the relationship between *P* and *N* changes? Please explain.

$P^2 = 4A_s$ (definition)

$$A_s = surface\ area$$

$$\Omega = surface\ area\ per\ atom$$

$$\therefore A_s = \Omega N$$

$$P^2 = 4\mathfrak{b}A_s = 4\mathfrak{b}\Omega N$$

$$P = 2\sqrt{\mathfrak{b}\Omega N}$$

For 2D growth, deposition occurs on the perimeter. The perimeter is where new interfaces are formed. In order to determine ΔG for the deposition, we need to know how the perimeter changes with the number of atoms in a cluster. This is a key aspect of the critical cluster size required for growth.

The free energy decrease due to the potential change is proportional to the number of atoms.

The free energy increase due to the formation of new interface scales with $\sqrt{N}$. Therefore, we eventually reach an N_{crit} where any additional atoms will decrease ΔG and stable growth is possible.

P is not a function of overpotential, and the relationship does not change.

However, the other term that contributes to ΔG is a function of potential, and therefore N_{crit} changes with potential.

Suppose that you are the engineer put in charge of implementing an electroplating plating process for your company. After considerable effort, you get the process running only to discover that the uniformity of the plating layer is not acceptable. Using Wa as a guide, and assuming that the solid phase is very conductive, describe three or four changes that you might try to improve plating uniformity. Please justify each recommended change.

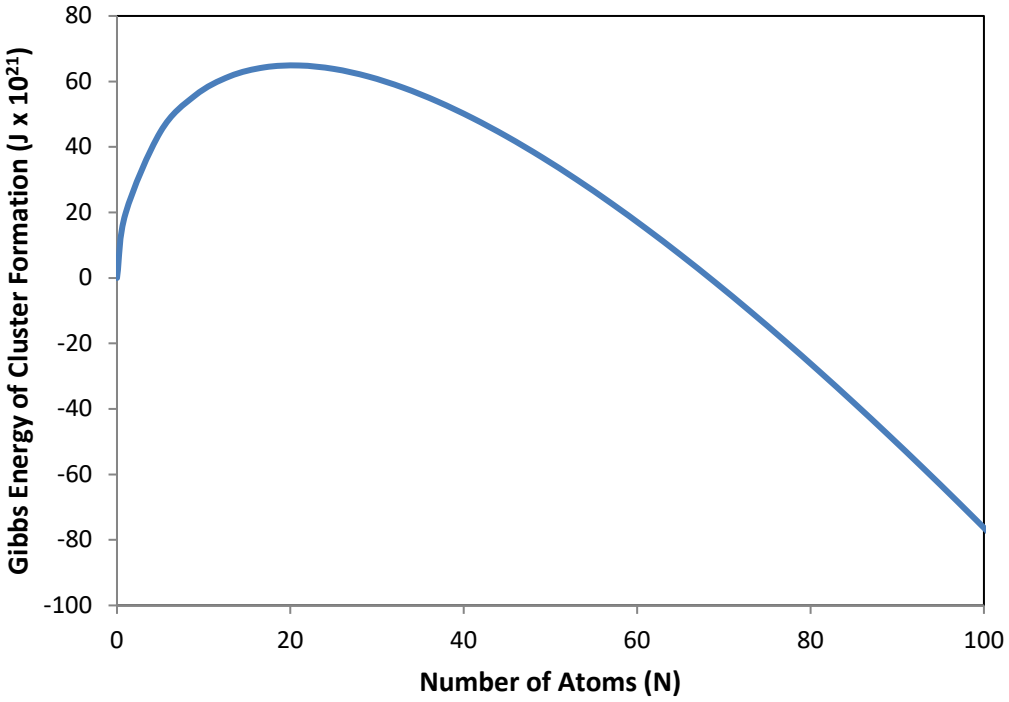
Spherical Nucleation

B	113.097336	36 pi
B^1/3	4.83597586	
Vm	1.26E-23	cm3
Vm^2/3	5.4183E-16	
sigma	1.00E-05	J/cm2
eta1	4.00E-02	V
z	1.00	
q	1.60E-19	C

Ncrit 20.3

$$N_{crit,3D} = \frac{8BV_m^2\sigma^3}{27(zq|\eta|)^3}$$

N	Term 1	Term 2	DG	DG, scaled
0	0.00E+00	0	0.00E+00	0.00
1	-6.41E-21	2.62026E-20	1.98E-20	19.79
5	-3.20E-20	7.66168E-20	4.46E-20	44.58
9	-5.77E-20	1.13372E-19	5.57E-20	55.70
13	-8.33E-20	1.44868E-19	6.16E-20	61.56
17	-1.09E-19	1.73238E-19	6.43E-20	64.30
21	-1.35E-19	1.99445E-19	6.49E-20	64.88
25	-1.60E-19	2.24029E-19	6.38E-20	63.83
29	-1.86E-19	2.4733E-19	6.15E-20	61.50
33	-2.11E-19	2.6958E-19	5.81E-20	58.12
37	-2.37E-19	2.90946E-19	5.38E-20	53.85
41	-2.63E-19	3.11554E-19	4.88E-20	48.83
45	-2.88E-19	3.31502E-19	4.31E-20	43.14
49	-3.14E-19	3.50866E-19	3.69E-20	36.87
53	-3.40E-19	3.6971E-19	3.01E-20	30.09
57	-3.65E-19	3.88086E-19	2.28E-20	22.83
61	-3.91E-19	4.06036E-19	1.51E-20	15.15
65	-4.17E-19	4.23597E-19	7.08E-21	7.08
69	-4.42E-19	4.40802E-19	-1.35E-21	-1.35
73	-4.68E-19	4.57677E-19	-1.01E-20	-10.11
77	-4.93E-19	4.74247E-19	-1.92E-20	-19.17
81	-5.19E-19	4.90532E-19	-2.85E-20	-28.52
85	-5.45E-19	5.06551E-19	-3.81E-20	-38.13
89	-5.70E-19	5.22321E-19	-4.80E-20	-47.99
93	-5.96E-19	5.37856E-19	-5.81E-20	-58.09
97	-6.22E-19	5.5317E-19	-6.84E-20	-68.41
101	-6.47E-19	5.68275E-19	-7.89E-20	-78.93

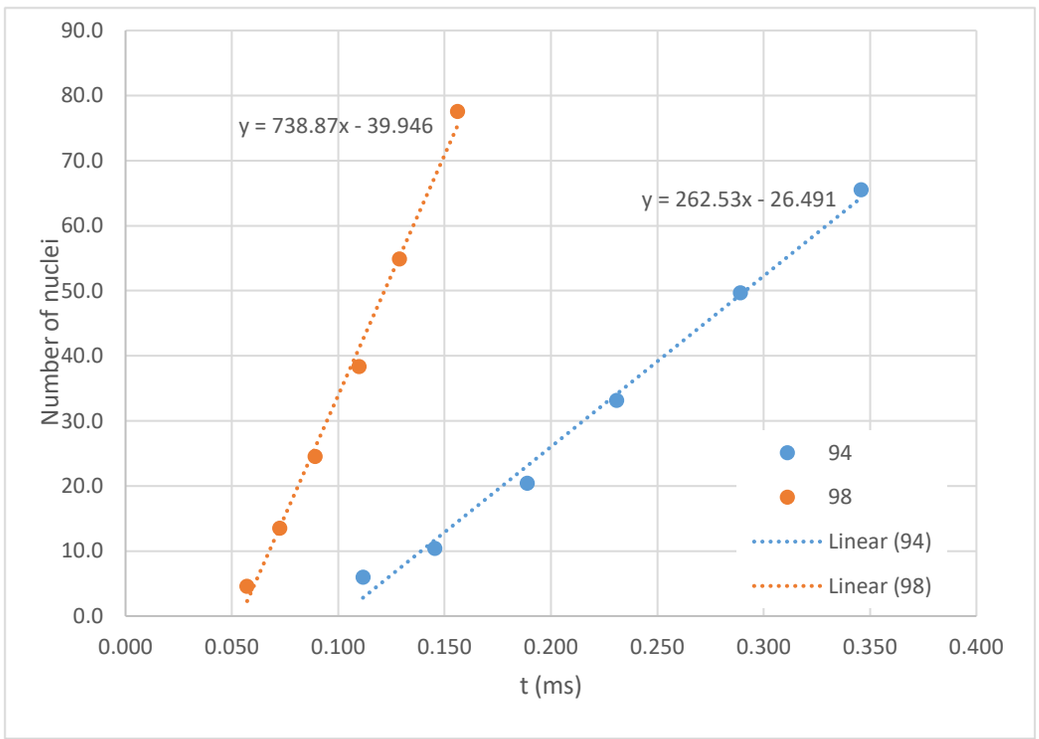

80
60
40
20
0
-20
-40
-60
-80
-100
Gibbs Energy of Cluster Formation (J x 10^21)
0
20
40
60
80
100
Number of Atoms (N)

The following data were taken for the number of nuclei as a function of time at the overpotentials indicated for the same system considered in Illustration 13-4, but over a different range of overpotentials. Please use these data to determine the nucleation rate at each of the two overpotentials given. Then, fit the nucleation rate data from these two points together with the data from the illustration to the expression for the 3D nucleation rate. Finally, estimate the critical value of the overpotential. How do your results compare to those from the illustration?

94 mV		98 mV	
t [ms]	Z_{nuc} [cm^{-2}]	t [ms]	Z_{nuc} [cm^{-2}]
0.112	6.0	0.057	4.6
0.145	10.5	0.072	13.6
0.189	20.5	0.089	24.6
0.231	33.2	0.110	38.4
0.289	49.7	0.129	54.9
0.346	65.6	0.156	77.6

Fit additional data

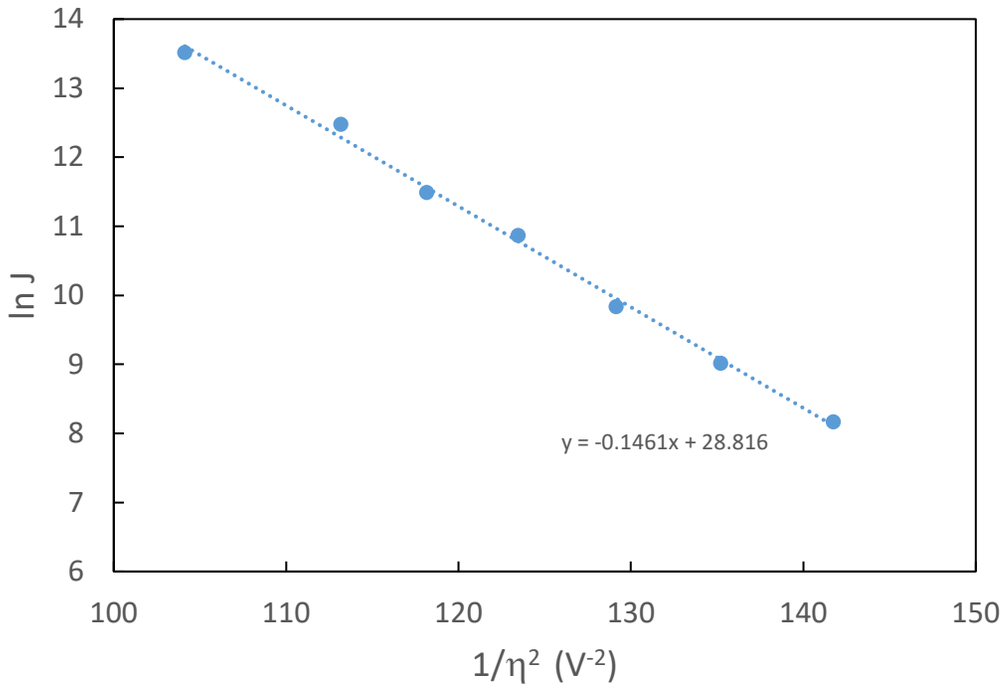
94 mV		98 mV	
t [ms]	Z_{nuc} [cm^{-2}]	t [ms]	Z_{nuc} [cm^{-2}]
0.112	6.0	0.057	4.6
0.145	10.5	0.072	13.6
0.189	20.5	0.089	24.6
0.231	33.2	0.110	38.4
0.289	49.7	0.129	54.9
0.346	65.6	0.156	77.6
slope	262530.6	slope	738870



Now add to previous data from Illustration 13-4

h	J
0.084	3532
0.086	8263
0.088	18735
0.090	52284
0.092	97477
0.094	262531
0.098	738870

$1/h^2$	ln J
141.723	8.16967178
135.208	9.019483715
129.132	9.838124177
123.457	10.8644512
118.147	11.48736757
113.173	12.47812279
104.123	13.51287776
slope	-0.14606415
intercept	28.8157768
A	3.26989E+12



Please derive the expression for *r* as a function of *t* for a growing hemispherical nucleus beginning with a mass balance similar to that given in equation 13-21. Compare the resulting relationship to that given for a 2D cylindrical nucleus in equation 13-23. Comment on similarities and differences between the two equations. What does the equation represent physically and what was a key assumption in its derivation?

$$\frac{dm_i}{dt} = \rho_i \frac{d\mathbb{V}}{dt} = \frac{M_i i_{\text{surf}}}{nF}(a) \qquad (13\text{-}21)$$

$$\rho_i(4\pi r^2)\frac{dr}{dt} = \frac{M_i i_{\text{surf}}}{nF}(4\pi r^2)$$

$$\frac{dr}{dt} = \frac{M_i i_{\text{surf}}}{\rho_i nF}$$

$$r = \frac{M_i i_{\text{surf}}}{\rho_i nF} t$$

This is the same equation as that derived for the 2D situation.

Key assumption $\Longrightarrow i_{surf} = const.$

This is how the radius changes with time due to a constant rate of reaction at the surface.

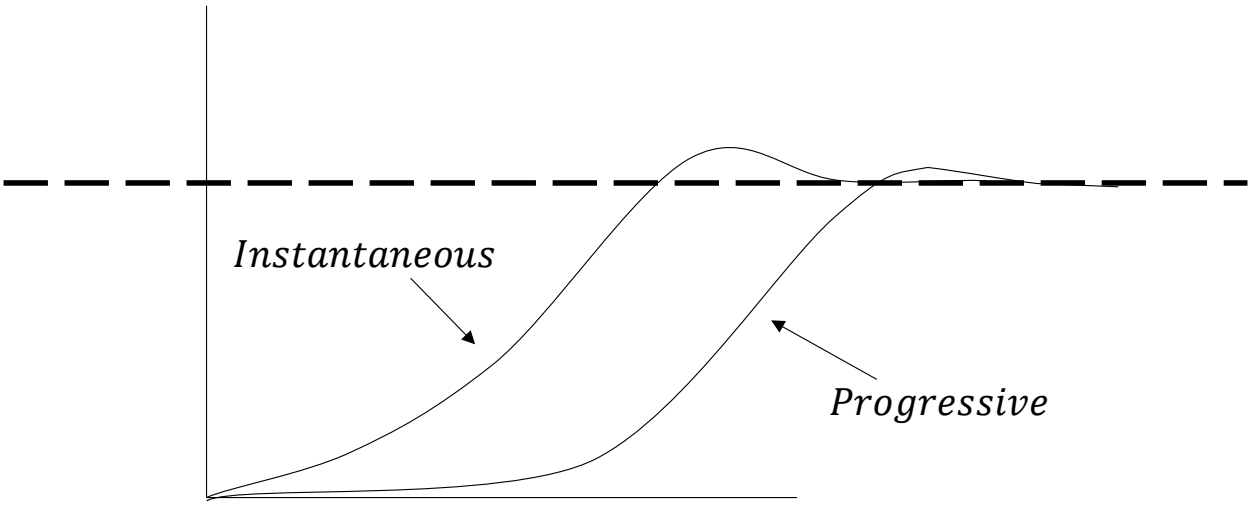
Implies that $\phi_{metal}\ and\ \phi_{solution}$ are constant.

Figure 13-10 shows current as a function of time for 2D layer growth under the assumptions of instantaneous and progressive nucleation.

a. In both cases, the current drops to zero at "long" times. Why?
b. Please sketch analogous curves for 3D nucleation and growth. How are they different? Why?

a. For 2D growth, growth moves outward along the perimeter only. It eventually goes to zero as the entire perimeter is consumed through overlap, and no "edge" area remains.

b.



They both reach the same limit as the entire surface has coalesced and continues to grow in one direction.

Assumes $i_{surf} = const.$

$\phi_m = const.$ $\phi_s = const$

Maximum occurs because rate depends on the surface area which reaches a maximum before full coalescence takes place.

In this problem, we examine instantaneous nucleation both with and without overlap.

a. Calculate the current as a function of time for 2D instantaneous nucleation without overlap and plot the results (t~10s). Assume a nucleation density of 4×10^{10} cm^{-2}. Assuming equally spaced nuclei, estimate the time at which you would expect overlap to occur.
b. Calculate the current as a function of time assuming overlap. Plot the results on the same figure as the data from part (a). Assume the same nucleation density. Based on the results, comment on the accuracy of the estimate made in part (a).

The following parameters are known (Ag): n = 1; M_{Ag} = 107.87 g mol^{-1}; ρ = 10.49 g/cm^3; i_{surf} = 0.005 A cm^{-2}; h = 0.288 nm.

2D

t	in mA I (No Overlap)	in mA I (Overlap)
0	0.00	0.00
0.5	9.64	9.56
1	19.29	18.61
1.5	28.93	26.70
2	38.57	33.44
2.5	48.21	38.58
3	57.86	41.96
3.5	67.50	43.60
4	77.14	43.58
4.5	86.79	42.13
5	96.43	39.52
5.5	106.07	36.04
6	115.71	32.02
6.5	125.36	27.76
7	135.00	23.49
7.5	144.64	19.43
8	154.29	15.72
8.5	163.93	12.44
9	173.57	9.64
9.5	183.22	7.32
10	192.86	5.44

Number of nuclei	4.00E+10	nuclei	
Total time	10	s	
Constant	4.82145E-16	2*pi*h*M*isurf^2/(rho*n*F)	
M	107.87	g/mol	
rho	10.49	g/cm3	
n	1		
F	96485	C/eq	
isurf	0.005	A/cm2	
h	2.88E-08	cm	

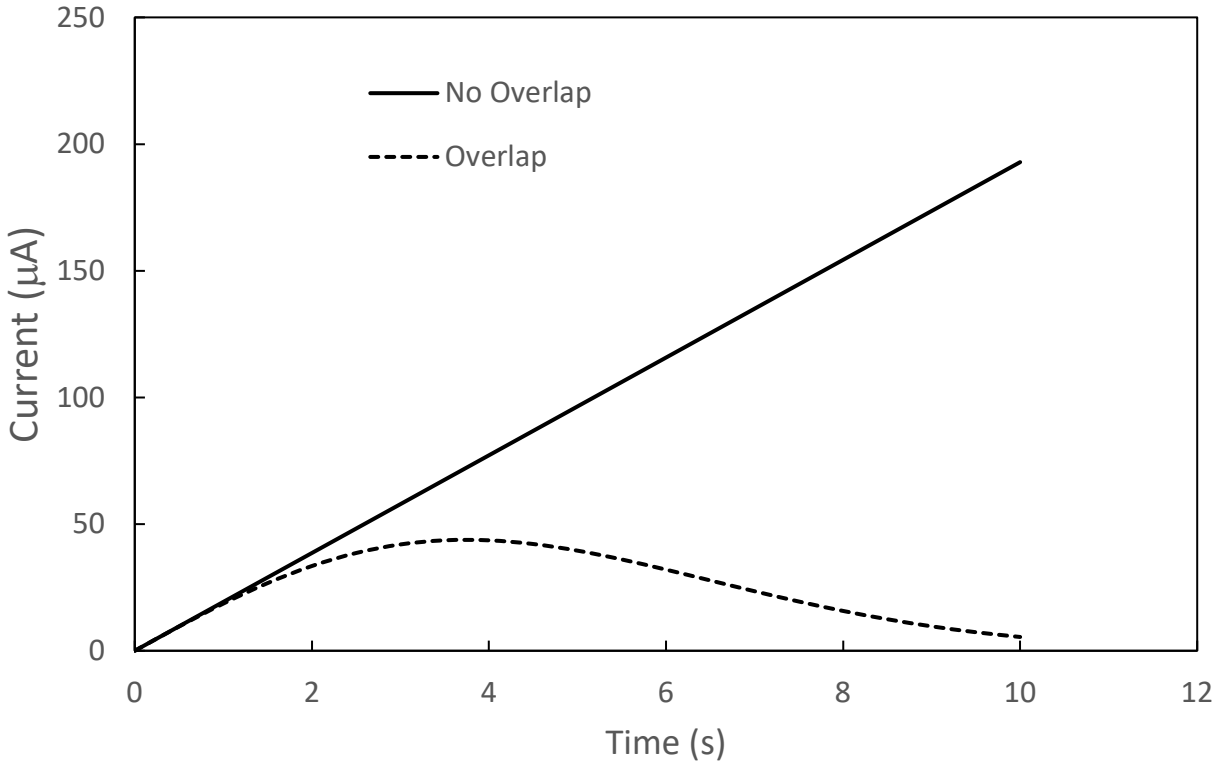
Approximate Time for overlap

Spacing	5.00E-06	cm	Evenly spaced nuclei
Time	4.69	s	

$$r = \frac{Mi_{surf}}{\rho nF} t$$

$$I = i_{surf}(2\pi rh) = \frac{2\pi hM\, {i_{surf}}^2}{\rho nF} t$$

$$I = \frac{2\pi hMN_0\, {i_{surf}}^2}{\rho nF} t\, exp\left(-\frac{\pi M^2 N_0 {i_{surf}}^2 t^2}{(\rho nF)^2}\right)$$



In the section on deposit morphology, we discussed the morphological development of deposits in terms of the fundamental processes that occur as discussed in previous sections.

a. Please re-read that section and comment briefly on the role of the overpotential in at least one aspect of deposit growth.
b. Assume that an additive is added to the solution that preferentially adsorbs and inhibits growth at step sites and kink sites. How might this affect deposit growth?

a) (Various responses are possible and acceptable- see section on deposit morphology) An example of a suitable response is the following:

As the overpotential is increased, nucleation becomes important and deposit growth is no longer dependent on existing growth sites. This leads to deposits with large numbers of crystal grains because of the additional sites available for deposit growth. The relative rates of nucleation and growth determine the number of crystals and hence the granularity of the deposit. A hard, rigid polycrystalline deposit may result if the small grains persist. In contrast, non-uniformities in the growth rate of different crystal planes can result in the formation of larger crystals as the deposit thickens, and may even lead to columnar deposits. Deposits with fewer large grains tend to be more ductile.

b) A higher overpotential will be needed, since the lower energy growth sites are blocked. Also, nucleation will be important and the overall growth may be more granular and more uniform across the surface.

Suppose that you are the engineer put in charge of implementing an electroplating plating process for your company. After considerable effort, you get the process running only to discover that the uniformity of the plating layer is not acceptable. Using Wa as a guide, and assuming that the solid phase is very conductive, describe three or four changes that you might try to improve plating uniformity. Please justify each recommended change.

$$\mathrm{Wa} = \frac{RT\kappa}{FL}\frac{1}{\left|i_{avg}\right|\alpha_c},$$

We need to increase Wa in order to increase uniformity.

1) Reduce the current density. This will increase your uniformity at the expense of your production rate. It is easy to do because you have direct control over the current density. This is the classical trade-off between production rate and the quality of the product.
2) Increase the conductivity. This may be done by adding a supporting electrolyte. The limiting case of this approach is to add excess supporting electrolyte, which will effectively eliminate ohmic losses. However, excess supporting electrolyte may actually reduce the quality and rate of deposition if the deposition becomes mass transfer limited. Mass transfer limited deposition may also be non-uniform.
3) Decrease L. This will reduce the solution resistance and, therefore, increase the relative kinetic resistance and Wa. The addition of multiple anodes is an example of a potentially effective way to reduce L, since each area of the work piece will have improved access to current by way of one or more of the additional anodes. However, reducing L may not improve uniformity if the reduction in spacing is not “uniform” across the work piece and causes one area to have significantly greater access than another.

Suppose that you are conducting tests on a plating bath with use of a Hull cell.

a. Assume that the bath does not plate uniformly. Where and under what conditions would you expect to see the highest deposition rate?
b. In measuring the local deposition rate, you find that the deposition rate on the surface closest to the anode is less than observed in the middle of the cathode. Please provide a possible explanation.

a) You would expect to see the highest deposition rate at the place on the cathode that is closest to the anode under the conditions where the solution resistance is important. If the solution resistance is not important, Wa will be greater than one and the current distribution will be nearly uniform.

b) One possible explanation is that a side reaction such as gas evolution takes place at that location. Under such conditions, the local current density could be higher (metal deposition + gas evolution) while the metal rate could be similar to or lower than that in the middle of the cathode due to the lower current efficiency and disruption of the metal deposition process by pronounced gas evolution.

A Haring-Blum cell is used to measure the throwing power of a plating bath. The distance ratio, x_1/x_2 is 5, and the conductivity of the solution is 20 S m^{-1}. The measured deposit loading at x_1 is 0.8 kg m^{-2}, and that at x_2 is 1.4 kg m^{-2}. Both electrodes have the same surface area. What is the throwing power?

$$\text{Throwing Power } (\%) = \frac{100(K-B)}{K+B-2}$$

$$K = \frac{x_1}{x_2} = 5$$

$$B = \frac{w_2}{w_1} = \frac{1.4\,\frac{kg}{m^2}}{0.8\,\frac{kg}{m^2}} = 1.75$$

$$\text{Throwing Power} = 100\,\frac{5-1.75}{5+1.75-2}$$

$$= 68.4\%$$

The throwing power is a measure of the ability of the solution to produce a uniform deposit under conditions where the solution resistance is different and known owing to the experimental cell.

Iron is electrodeposited from a bath that is 0.5 M in Fe^{2+} at a pH of 5. The anode is also iron, and the potential applied across the cell is -3.0 V. Due to the larger size and surface area of the anode, the anodic surface overpotential can be neglected for this problem, as it was in the illustration (not true in general); concentration gradients can also be neglected. However, *iR* losses in solution are important. Because of this, the current density is not uniform. We are interested in the relative deposition rate at two specific points on the surface, and the impact of the side reaction (hydrogen evolution) on that relative rate, as well as on the current efficiency. The solution resistance from the anode to the cathode is 0.005 Ω-m^2 at the first point of interest, and 0.006 Ω-m^2 at the second. Please determine the value of the current density at each of the two points, as well as the relative rate of deposition. Next, include the hydrogen reaction and repeat the calculation. In this example, how did H_2 evolution impact the absolute and relative rates of deposition? The following parameters are known:

Iron reaction: Tafel slope ≈ -0.1 V; i_o = 0.8 A m^{-2}
Hydrogen evolution reaction: Tafel slope: -0.11 V; $i_o = 10^{-2.3}$ A m^{-2}

	0.5	M	Fe electrode
ts	-0.1		
io	0.8	A/m2	
Uni	-0.4489		

ts	-0.11		H2 kinetics
io	5.01E-03	A/m2	
pH	5		
Uh	-0.296		

Without side reaction, the problem is easily solved with a spreadsheet

			R (Ohm m2	i (A/m2)	IR loss (V)	Vtot (no H2	Solve Block	V kinetic
Voltage (Fe ref)		point 1	5.00E-03	543.4	2.717	-3	6.03009E-09	-0.2832
-3		point 2	6.00E-03	454.1	2.725	-3	6.01499E-09	-0.2754
				1.197				

Use Python to solve problem with side reaction

			R (Ohm m2	i (A/m2) Fe	i(A/m2) H2	Current Efficiency	
Voltage (Fe ref)		point1	5.00E-03	501.1	42.9	92.11	
-3		point2	6.00E-03	418.3	36.4	91.99	
				1.198			

Electrodeposition is to be performed on a thin chrome layer that has been deposited on an insulating substrate. The layer is 0.5 □m thick and of uniform thickness. About how far from the point where electrical connection is made can electrodeposition be performed (distance L) if the current density across the surface must not vary by more than 20%? The solution phase is not limiting. Assume that the conductivity of the chrome is equal to its bulk value and α_c = 0.5. The average current density is 200 A/m^2.

This problem is similar to Illustration 13-7, except that we are solving for the length rather than the thickness.

Solution: Application of equation 13-46 at the two ends of the resistive substrate (x = 0 and x = L) must yield current densities that differ by no more than 20%. Therefore,

$$\frac{i_n(0)}{i_n(1)} = \frac{2\theta^2\chi\sec^2(\theta(0-1))}{2\theta^2\chi\sec^2(\theta(1-1))} = \frac{\sec^2(-\theta)}{\sec^2(0)} = \sec^2(\theta) = 1.20$$

Solving this expression for θ yields $\theta = 0.42053$. We can now use this value of θ in equation 13-44b to find χ

$$\chi = \frac{1}{2\theta\tan\theta} = 2.6586$$

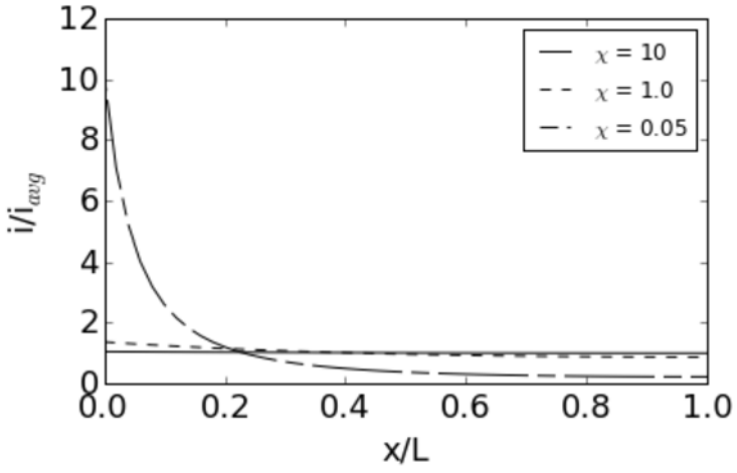
From the definition of χ

$$\chi = \frac{RT\sigma\delta}{|i_{avg}|L^2\alpha_c F}$$

$$L = \sqrt{\frac{RT\sigma\delta}{|i_{avg}|\chi\alpha_c F}} = \sqrt{\frac{(8.314)(298.15)(7.9\times10^4)(5.0\times10^{-5})}{(0.200)(2.6586)(0.5)(96485)}} = 0.618 \text{ cm}$$

Problem 13.18

In [4]:
```
from matplotlib.pyplot import *
from matplotlib.lines import *
from scipy.optimize    import *
from numpy             import *
%matplotlib inline

X = [100,10,1,.1,.05]
x = linspace(0,1,51);
#x = 1

theta = [0,0,0,0,0]

def solverF(xx,j):
    F=tan(xx)-1/(2*xx*X[j])
    return F

for i in range (5):
    xGuess = pi/4
    theta[i] = fsolve(solverF,xGuess,i)

y0=2.*theta[0]**2*X[0]*(1/cos(theta[0]*(x-1)))**2;
y1=2.*theta[1]**2*X[1]*(1/cos(theta[1]*(x-1)))**2;
y2=2.*theta[2]**2*X[2]*(1/cos(theta[2]*(x-1)))**2;
y3=2.*theta[3]**2*X[3]*(1/cos(theta[3]*(x-1)))**2;
y4=2.*theta[4]**2*X[4]*(1/cos(theta[4]*(x-1)))**2;

plot(x,y1,'k-',label= r'$\chi$ = 10');
plot(x,y2,'k--',label= r'$\chi$ = 1.0');

line, = plot(x,y4,'k--',label= r'$\chi$ = 0.05');
dashes = [10, 5, 50, 5] # 10 points on, 5 off, 100 on, 5 off
line.set_dashes(dashes)
legend(prop={'size':12})
xlabel('x/L');
ylabel(r'i/i$_{avg}$');
rc("font",size=18)
gcf().subplots_adjust(bottom=0.20)

savefig('figure.jpg')
```



In [ ]:

Copper is to be electrodeposited onto a thin copper seed layer, 20 nm thick, which has been deposited onto a silicon oxide insulator. If the solution-phase conductivity is high, how much would you expect the deposition current to vary over a 150 mm distance if the average current is 10 A m^{-2}? Assume that the conductivity of the copper is the same as its bulk conductivity. Thin layers often have conductivities that are significantly lower than the bulk value. Comment on the impact of the conductivity on the results reported above.

L	15	cm
delta	2.00E-06	cm
alpha	0.5	
iave	0.001	A/cm2
sigma_cu	5.96E+05	S/cm
F	96485	C/eq.
R	8.314	J/mol K
T	298.15	K

$$\chi = \frac{RT\sigma\delta}{|i_{avg}|L^2\alpha_c F}$$

chi **2.722E-01**

$$\frac{di^*}{dx^*} = \frac{i_n(x^*)}{i_{avg}} = 2\theta^2\chi\sec^2(\theta(x^* - 1))$$

in(0)= 2 theta^2 chi sec^2 (-theta)
in(1)= 2 theta^2 chi sec^2 (0)

ratio = sec^2 (-theta)/sec^2(0) = sec^2(-theta)

Find theta

$$\chi = \frac{1}{2\theta\tan\theta}$$

theta	1.0510531	
chi	0.2722131	
solver	-1.578E-07	Use solver to find theta

Ratio of rate
4.05403

The initial deposition rate will vary by a factor of 4 over the 150 mm length.
If the conductivity were an order a magnitidue lower, it makes a large difference.

The initial depositon rate will vary by more than 150X. This is clearly a factor to consider.

Electrodeposition is being performed onto a thin metal layer (σ = 6 x 10^6 S m^{-1}) that has been deposited onto an insulating substrate. The length scale associated with solid phase (distance from connection point) is 0.5 m, and the thickness of the solid layer is 100 nm. The conductivity of the solution is 20 S m^{-1}, and the length scale associated with the solution transport is 0.1 m. The average current density is 500 A m^{-2}. Would you expect the current distribution to be uniform? If not, which phase (solution, solid, or both) would determine the non-uniform current distribution? In which direction would the thickness of the metal layer need to change in order to change the limiting process?

R	8.314	J/mol K
T	298.15	K
F	96485	C/eq
s	6.00E+06	S/m
k	20	S/m
d	1.00E-07	m
L_{solid}	0.50	m
L_{elect}	0.1	m
i_{ave}	500	A/m2
c	2.47E-04	
Wa	0.020553	
Ratio	1.20E-02	

$$\chi = \frac{R_{ct}}{R_{sub}} = \frac{RT\sigma\delta}{|i_{avg}|L^2\alpha_c F}$$

$$\mathrm{Wa} = \frac{RT\kappa}{FL}\frac{1}{|i_{avg}|\alpha_c},$$

The substrate resistance is limiting. Therefore, the metal layer would need to be thicker in order to change the limiting factor.

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Problem 14-1

$T = 298$ [K]

$R = 8.314$ [J/K-mol]

$F = 96485$ [coulomb/mol]

$Up = 1.3595$ [V]

$Un = -0.828$ [V]

$Vc = Up - Un$

$MW = 0.039997$ [kg/mol]

$m = 1$ [kg]

$n = 1$

$$se = Vc \cdot m \cdot n \cdot \frac{F}{MW}$$

$cf = 3600$ [J/W-h]

$$se1 = \frac{se}{cf \cdot m}$$ *theoretical value based on standard potentials*

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cf = 3600 [J/W-h]
m = 1 [kg]
n = 1
se = 5.277E+06 [J]
T = 298 [K]
Up = 1.36 [V]

F = 96485 [coulomb/mol]
MW = 0.04 [kg/mol]
R = 8.314 [J/K-mol]
se1 = 1466 [W-h/kg]
Un = -0.828 [V]
Vc = 2.188 [V]

No unit problems were detected.

Problem Statement:

What is the minimum energy required to produce a kg of NaOH from a brine of NaCl? Compare this number with typical values reported industrially of 2100-2500 Wh/kg. What are some factors that account for the difference? A rule of thumb for the chlor-alkali industry is that 2/3 of the production costs are electrical energy. If the cost of electricity is $0.06/kWh, estimate the cost to produce a kg of Cl_2.

Cost Estimation:

The theoretical value of 1466 $\frac{W \cdot h}{kg}$ is much lower than the practical values of $2100 - 2500$ $\frac{W \cdot h}{kg}$

To estimate Cl_2 cost, use 2300 $\frac{W \cdot h}{kg}$

$$\frac{2300\ W \cdot h}{kg} \left| \frac{\$0.06}{kW \cdot h} \right| \frac{kW}{1000W} \left| \frac{3\ total}{2\ electricity\ cost} \right.$$

$$= \$\frac{0.21}{kg} \text{ to produce } Cl_2$$

The third and most modern design for the chlor-alkali process uses an ion-exchange membrane instead of the porous diaphragm. The membrane allows cations to permeate through but is an effective barrier for anions and water. How would the cell design change for this approach? Identify possible advantages and disadvantages to the membrane design.

Use of an ion-exchange membrane effectively separates the two compartments and permits the electrodes to be much closer. Cells can be stacked and connected in either a monopolar or bipolar fashion. High purity streams are possible.

Advantages:

1. Lower cell voltage due to “zero gap cells” made possible by the membrane. This translates into lower energy costs.
2. Higher efficiency due to minimal crossover.
3. No Hg (relative to mercury cells, which are being phased out due to environmental concerns related to Hg).
4. High purity products.

Disadvantages:

1. Cost of ion-exchange membrane.
2. Membrane lifetime.
3. Increased sensitivity to impurities in the brine— requires brine purification.

An alternative chlor-alkali process has been proposed. Rather than evolving hydrogen, the cathode for a membrane cell design is replaced with an oxygen electrode. Write the cathodic reaction at the oxygen electrode. Compare the equilibrium potential and theoretical specific energy for Cl_2 production with that for the conventional cell. What are some advantages and challenges with this concept?

$O_2\ Reaction$:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$U = 1.229 - 0.0592(pH)$

$= 1.229 - 0.0592(14)$

$= 0.400\ V$

Use standard potential for Cl_2 as estimate.

$Cell\ potential = 1.3595 - 0.400 = 0.960$

This cell potential is lower.

Theoretical specific energy

$$SE = \frac{(nF)U_{cell}}{MW}$$

$$= \frac{(0.960V)\left(2\frac{equiv}{mol}\right)\left(96485\frac{C}{equiv}\right)}{0.039997\frac{kg}{mol}}$$

$$= \frac{\left(0.960\frac{J}{C}\right)\left(\frac{2\ equiv}{mol}\right)\left(96485\frac{C}{equiv}\right)W \cdot h}{\left(0.039997\frac{kg}{mol}\right)(3600s)(\frac{J}{s})}$$

$$= 1287\frac{W \cdot h}{kg}$$

While the theoretical energy required is lower, O_2 would need to be supplied, and mass transfer limitations would be a problem. Would not have H_2 product.

HCl (g) is a waste-product in a number of chemical processes. Ideally, the HCl could be converted to Cl_2(g) economically. There are several paths to do this conversion including the Deacon process, which is not electrochemical. You are investigating the direct conversion of anhydrous HCl in an electrochemical cell analogous to a proton exchange membrane fuel cell. A proton conducting membrane serves as the separator and electrolyte. Write the overall and electrode reactions for this process. What is the equilibrium potential?

Reactions

$2HCl(g) \rightarrow Cl_2 + 2H^+ + 2e^-$ (anode)

$2H^+ + 2e^- \rightarrow H_2$ (cathode)

$2HCl(g) \rightarrow Cl_2 + H_2$ (overall)

$$\Delta G_{reac} = \frac{2(-95.3)kJ}{mol}$$

$$U_{cell} = \frac{-\Delta G}{nF} = \frac{(2)(95.3)(1000)}{2(96485)} = -1.98V$$

Negative indicates that it does not take place spontaneously.

By our normal convention $U_{cell} = U_{pos.} - U_{neg.}$

$U_{cell} = 1.98V$

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"!Problem 14-5"

T=298 [K]
R=8.314 [J/K-mol]
F=96485 [coulomb/mol]

G_co2=-394359 [J/mol]
G_alo=-1582300 [J/mol]

se1=(3*G_co2-2*G_alo)/MW/2/cf

MW=0.02698 [kg/mol]; "molecular weight of Al"
eta=0.3

cf=3600 [J/W-h]

pr=2.2 [$/kg]

ce=eta*pr*cf2/se1

cf2=1000 [W-h/kW-h]

SOLUTION
Unit Settings: SI C kPa kJ mass deg

ce = 0.0647 [$/kW-h]
cf2 = 1000 [W-h/kW-h]
F = 96485 [coulomb/mol]
G_{co2} = -394359 [J/mol]
pr = 2.2 [$/kg]
se1 = 10201 [W-h/kg]

cf = 3600 [J/W-h]
η = 0.3
G_{alo} = -1.582E+06 [J/mol]
MW = 0.02698 [kg/mol]
R = 8.314 [J/K-mol]
T = 298 [K]

No unit problems were detected.

Note on feasibility:

This is the break even point. Obviously, you would want a price for electricity lower than this so that you can make a profit.

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"!Problem 14-6"

eta_e=eta_f*U/V
U=1.22 [V]
V=4.19 [V]
eta_f=0.92

SOLUTION

Unit Settings: SI C kPa kJ mass deg

η_e = 0.2679
U = 1.22 [V]

η_f = 0.92
V = 4.19 [V]

No unit problems were detected.

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"!problem 14-7"

F=96485 [coulomb/mol]

i=900 [A/m^2]
b=2e10 [kg/yr]
pr=b/cf1
cf1=(365*24*3600) [s/yr]
n=3
MW=0.029 [kg/mol]

pr=i*A/(n*F)*MW*eta_f
eta_f=0.96

"CO2 evolved"

c=b*(44/29)*(3/4)

SOLUTION
Unit Settings: SI C kPa kJ mass deg

A = 7.326E+06 [m^2]	b = 2.000E+10 [kg/yr]
c = 2.276E+10 [kg/yr]	cf1 = 3.154E+07 [s/yr]
η_f = 0.96	F = 96485 [coulomb/mol]
i = 900 [A/m^2]	MW = 0.029 [kg/mol]
n = 3	pr = 634.2 [kg/s]

No unit problems were detected.

Problem 14-8

Start with the definition provided by Equation 14-1.

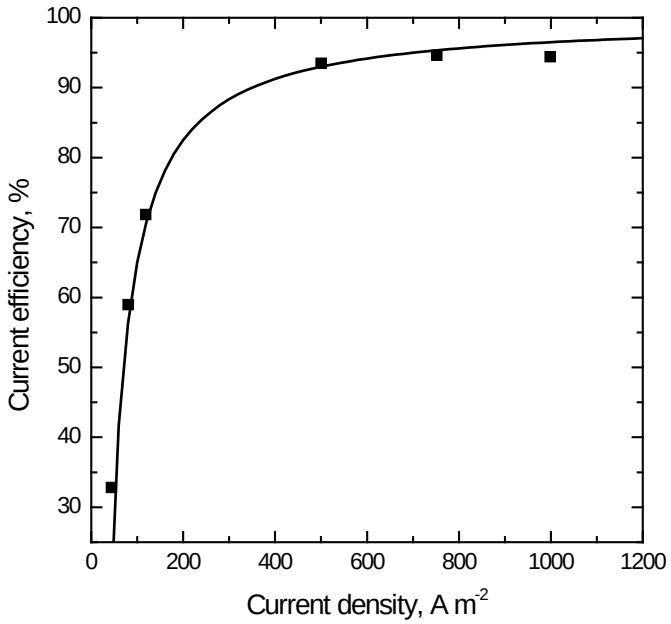
$$\eta_f = \frac{\text{mass of desired product recovered}}{\text{theoretical mass from Faraday's law}} = \frac{m_i}{QM_i / nF} = \frac{\dot{m}_i}{IM_i / nF} \tag{14-1}$$

$$\eta_f = \frac{IM_i/nF - x}{IM_i/nF} = 1 - xnF/iAM_i$$

write as

$$\eta_f = 1 - \frac{B}{i}$$

where B is a constant and A is the area of the electrode. The data are then plotted and the equation above used to make a prediction of efficiency. The line in the figure is for B=35 and it provides a decent fit of the data. Therefore, the data do support the model. Because the area is not provided, the value of x cannot be determined.



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"!Problem 14-9 AND TEXT"

"i=2700 [A/m^2]"
"i=1940 [A/m^2]"
"Vcell=3.45 [V]"

ioa=10 [A/m^2]
alpha_a=2

R=8.314 [J/mol-K]
T=333 [K]
F=96485 [coulomb/mol]

i=ioa*exp(alpha_a*F*eta_a/R/T)

ioc=0.07 [A/m^2]
alpha_c=1
i=ioc*exp(alpha_c*F*eta_c/R/T)

U=2.25 [V]; "equilibrium potential at cell conditions"

Vcell=U+eta_a+eta_c+eta_d+eta_s+eta_hw

Rd=2.222e-4 [ohm-m^2]
eta_d=Rd*i

Rs=1.111e-4 [ohm-m^2]
eta_s=Rs*i

Rhw=9.63e-5 [ohm-m^2]
eta_hw=Rhw*i

It=Ac*i

It=1e6 [A]

cost=A*Ac+B*(Vcell)
A=0.01 [1/m^2]
B=5 [V]

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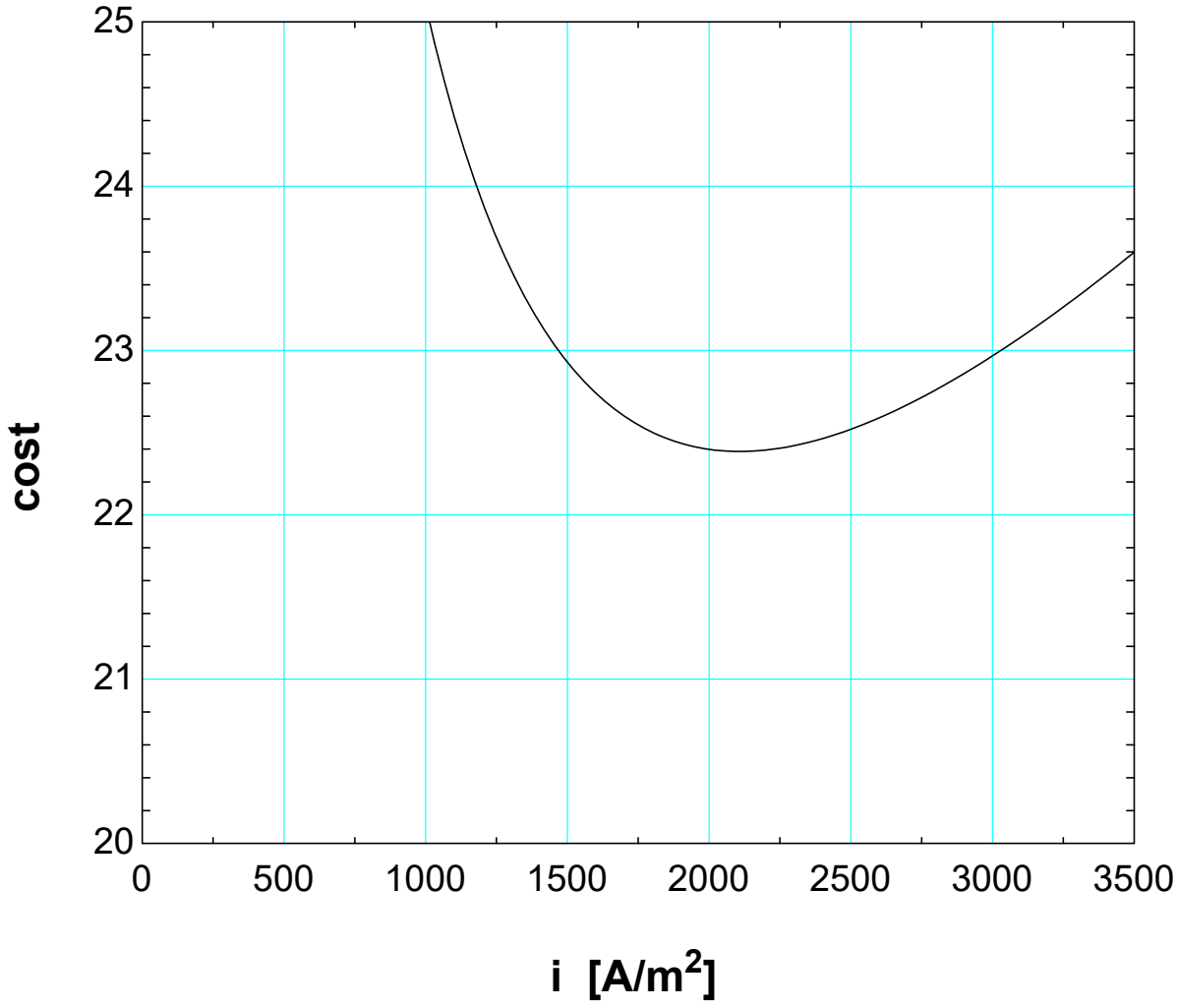

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PROBLEM 14-10

Determine optimum thickness of gap

find thickness where resitance is minimized

much of info comes from Hine, p. 175 for hooker cell

$$R_\Omega = \frac{h}{\kappa_{eff}}$$

h=0.01 [m]

$\kappa = 50$ [1/(Ω-m)]

$$\kappa_{eff} = \kappa \cdot \left(1 - \varepsilon_g\right)^{1.5}$$

superficial velocity at top

$$Vsg = \frac{I}{n \cdot F} \cdot R \cdot \frac{T}{p} \cdot 0.5 \cdot \frac{L}{h}$$

$L = 1$ [m] *assume height of electrode*

$p = 150000$ [Pa] *pressure of operation*

$R = 8.314$ [J/mol-K]

$T = 370$ [K]

$n = 2$

$F = 96485$ [coulomb/mol]

$I = 1250$ [A/m^2]

Estimate slip velocity, m/s

Assume stokes flow

$$vs = 0.5 \cdot 9.807\ [m/s^2] \cdot db \cdot db \cdot \frac{drho}{18 \cdot \mu}$$

$db = 0.0003$ [m]

$drho = 950$ [kg/m^3]

$\mu = 0.001$ [Pa-s]

use half value, i.e. midpoint when varying gap width

$$\varepsilon_g = 0.5 \cdot \frac{Vsg}{vs}$$

$$\eta_\Omega = R_\Omega \cdot I$$

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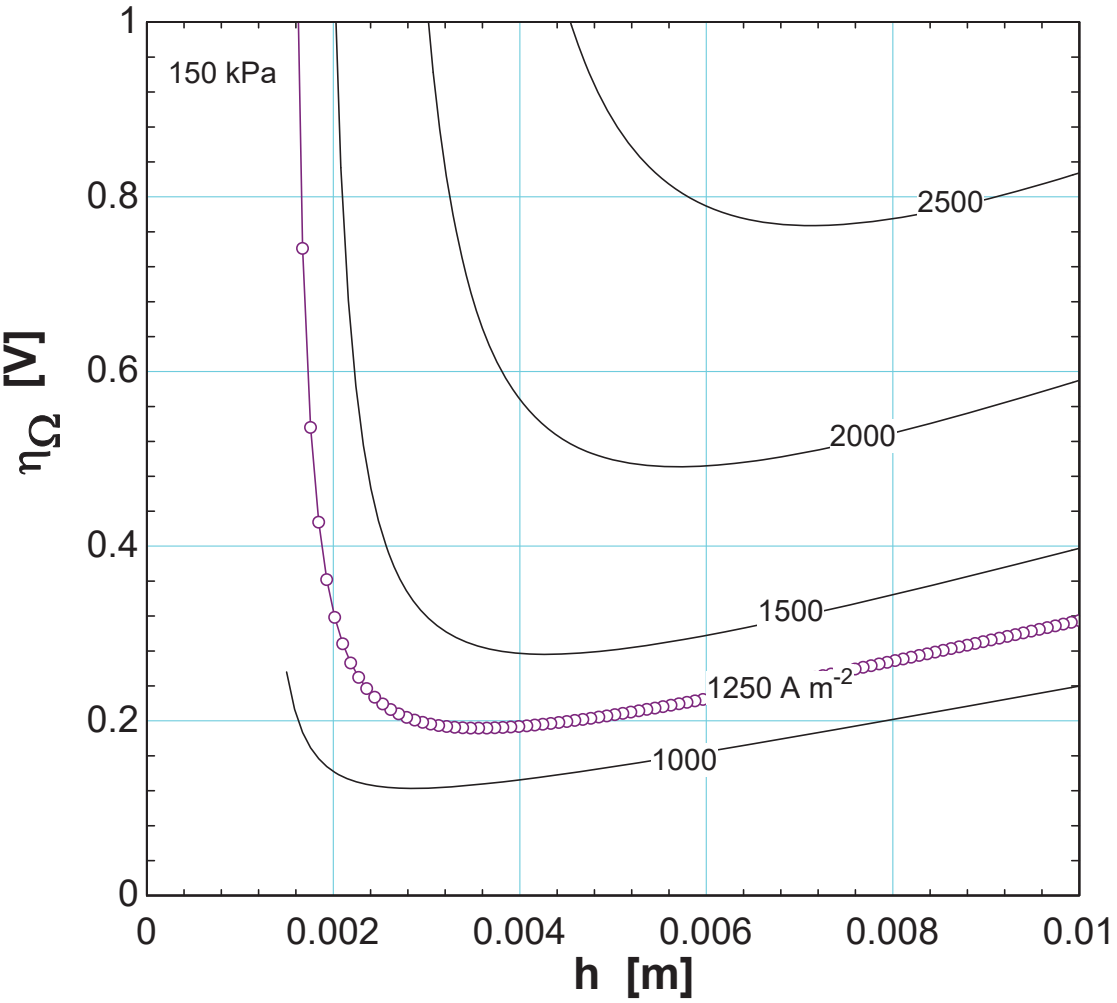

Run at 1250 A/m^2 with a gap of approximately 3.2 mm.

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"!PROBLEM 14-11"

pr=35000e3 [kg/yr]
eta_c=0.95
n=2
M=0.07091 [kg/mol]
F=96485 [coulomb/mol]
cost=0.06 [$/kW-h]

"m_dot=pr*cf1"

"Use Farday's law to convert production rate to coulombs"
Q=n*F*(pr/eta_c)/M
DELTAV=0.001 [V]

DELTAE=Q*DELTAV

cf1=3600000 [J/kW-h]
cf2=1000 [kg/ton]

dollar=cost*(DELTAE/cf1)

unitprice=cf2*dollar/pr

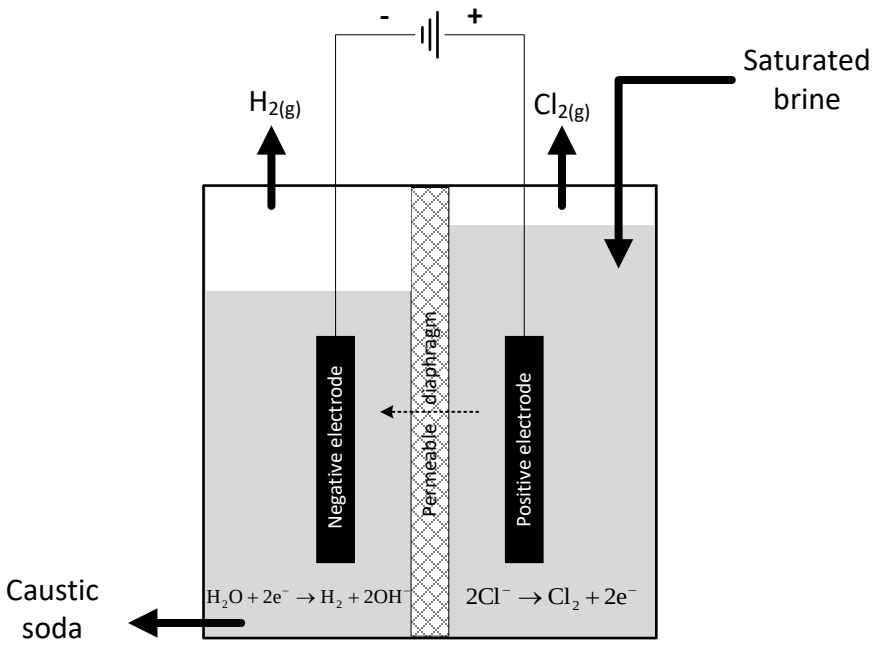
"For this one plant, the DSA technology could result in savings of 1.6 million dollars per year"

SOLUTION
Unit Settings: SI C kPa J mass deg
cf1 = 3.600E+06 [J/kW-h]
cf2 = 1000 [kg/ton]
cost = 0.06 [$/kW-h]
ΔE = 1.003E+11 [J/yr]
ΔV = 0.001 [V]
dollar = 1671 [$/yr]
η_c = 0.95
F = 96485 [coulomb/mol]
M = 0.07091 [kg/mol]
n = 2
pr = 3.500E+07 [kg/yr]
Q = 1.003E+14 [coulomb/yr]
unitprice = 0.04774 [$/ton]

No unit problems were detected.

Problem 14-12

Start with Figure 14-1 that shows the diaphragm process.



The following nomenclature is used, quantities highlighted are either known or specified

$\dot{m}_b$	flow of brine entering anode, kg h^{-1}
$\dot{m}_C$	mass flow of caustic leaving cathode, kg h^{-1}
$\dot{m}_D$	flow rate through the diaphragm, kg h^{-1}
I	current of process, A
PR	specified production rate of chlorine, kg h^{-1}
ρ_b	mass fraction NaCl in brine feed, assumed saturated
ρ_a	mass fraction NaCl in anode
ρ_{NaOH}	mass fraction caustic in cathode
ρ_{Cl_2}	mass fraction of Cl_2 in brine, assumed saturated
M_i	molecular weight of species kg mol^{-1}
η_f	faradaic efficiency defined by Equation 14.1 for production of Cl_2

Problem 14-12

The current can be determined from the rate of production and the faradaic efficiency, Equation 14.1

$$\eta_f = \frac{\text{rate of production of } Cl_2}{IM_{Cl_2}/nF} = \frac{PR(2F)}{IM_{Cl_2}}$$

No information is provided about competing reactions for H_2 and Cl_2 evolution, assume the loss in faradaic efficiency is from dissolved Cl_2 that flow into cathode chamber

$$\eta_f = \frac{PR}{PR + \dot{m}_D \rho_{Cl_2}}$$

Material Balances, steady state is assumed, no information about the current efficiency for NaOH or hydrogen is provided, assume a value of unity:

$$\text{in} - \text{out} + \text{generation} - \text{consumption} = 0$$

overall mass $$\dot{m}_b - PR - \dot{m}_C - \frac{IM_{H_2}}{2F} 0$$

cathode mass $$\dot{m}_D - \frac{IM_{H_2}}{2F} - \dot{m}_C = 0$$

These equations show that, as expected, the three flowrates are closely related.

Three additional species balances are made,

elemental chlorine on anode side

$$\dot{m}_b \rho_b \left(\frac{M_{Cl}}{M_{NaCl}}\right) - PR - \dot{m}_D \left(\rho_{Cl_2} + \rho_a \left(\frac{M_{Cl}}{M_{NaCl}}\right)\right) = 0$$

overall elemental Cl

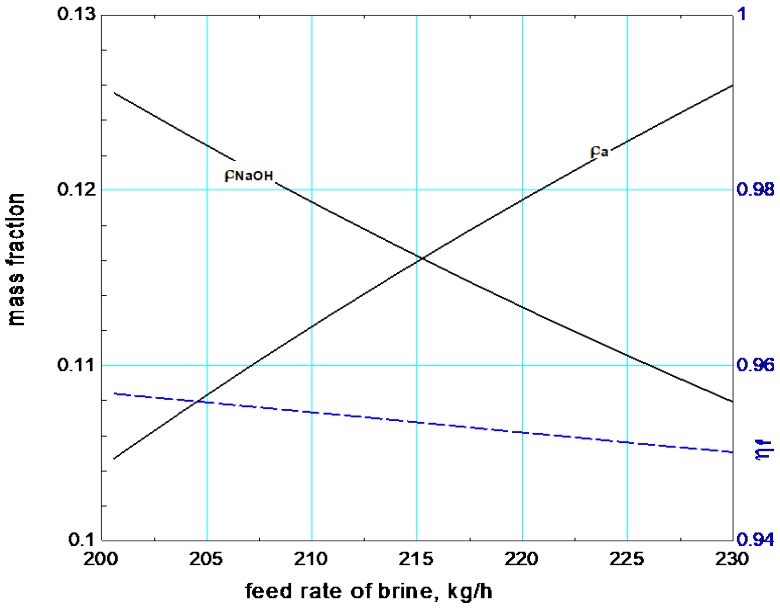
$$\dot{m}_b \rho_b \left(\frac{M_{Cl}}{M_{NaCl}}\right) - \text{PR} - \dot{m}_C \rho_{NaCl} \left(\frac{M_{Na}}{M_{NaCl}}\right) = 0$$

overall Na

$$\dot{m}_b \rho_b \left(\frac{M_{Na}}{M_{NaCl}}\right) - \dot{m}_C \rho_{NaOH} \left(\frac{M_{Na}}{M_{NaOH}}\right) - \dot{m}_C \rho_{NaCl} \left(\frac{M_{Na}}{M_{NaCl}}\right) = 0$$

Problem 14-12

These equations are solved simultaneously. The flowrate of brine is used as a parameter. In the figure shown below, it is assumed that the mass fraction of dissolved chlorine was 0.005 and that the brine feed was 26.5 % NaCl. The model is highly simplified, but does show relevant trends. As the feed rate of brine is increased, the concentration of NaOH produced decreases. We also see that the faradaic efficiency decreases. The decrease is simply a result of greater flow across the diaphragm, which transports results in more loss of Cl_2. Of course this model doesn't consider the effect of concentration on electrode polarizations. For instance, as the feed rate is reduced, the concentration of NaCl in the anode compartment decreases.



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PROBEM 14-13

$\kappa = 5$ [1/(Ω-m)]

$L = 0.5$ [m]

h=0.004 [m]

$p = 150000$ [Pa]

$vb = 0.006$ [m/s]

$n = 2$

$F = 96485$ [coulomb/mol]

$T = 308$ [K]

$R = 8.314$ [J/(mol-K)]

V=1 [V]

$$i_{avg} = V \cdot \kappa \cdot \left[\frac{4 + K}{h \cdot (2 + K)^2}\right]$$

$i_{avg} = 200$ [A/m^2]

$$K = R \cdot T \cdot \kappa \cdot L \cdot \frac{V}{n \cdot F \cdot p \cdot h \cdot h \cdot vb}$$

$$\varepsilon = \frac{K}{2 + K}$$

$$\kappa_{eff} = \kappa \cdot \left[\frac{4 + K}{(2 + K)^2}\right]$$

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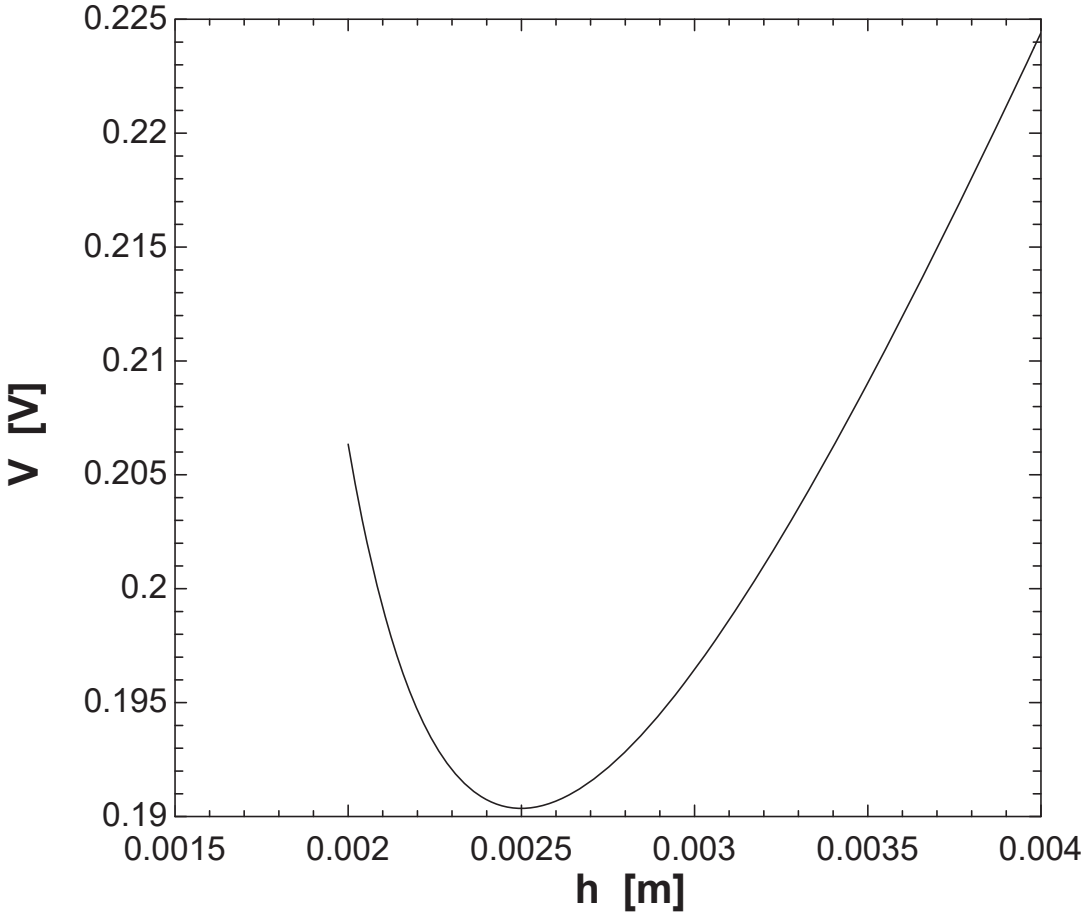


Summary:

Reducing the gap to 2mm is helpful relative to 4mm. However, the optimum is ~2.5mm, which would be the recommended gap size.

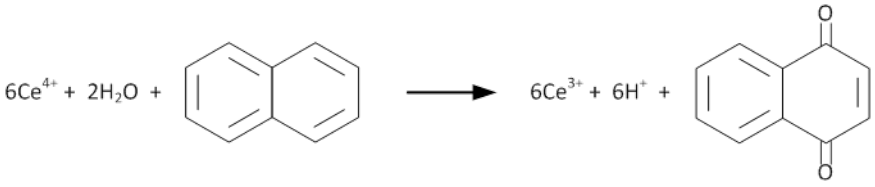
Problem 14-12

a) <u>electrorefining of tin</u>: in the electrorefining process, metal is oxidized at one electrode and deposited at the other. Ideally, there would be no concentration gradient and mixing is used to reduce variations in concentration. There is no need to use a divided cell in this instance.

reaction $\mathrm{Sn^{2+} + 2e^- \leftrightarrow Sn}$

A bipolar plate configuration is not feasible for two reasons. First, the electrodes must be removed frequently so an arrangement that allows easy removal and installation of electrodes is needed and further one that allows this replacement without disrupting is the entire process is desired. Second, because metal is being removed and redeposited the electrode dimensions will change, this is also not practical for a bipolar configuration.

b) <u>production of naphthoquinone</u> from naphthalene



in the process cerium acts as a mediator, and Ce^{3+} is oxidized at the anode. In this instance, an undivided cell is required. A bipolar configuration is feasible since there are no changes in the shape of the electrodes.

c) <u>redox flow battery</u>: use the example from section 14.8. The two reactions are

$$\mathrm{V^{3+} + e^- = V^{2+}} \qquad (14\text{-}26)$$

$$\mathrm{VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O} \qquad (14\text{-}27)$$

If the anolyte and catholyte are mixed, the reactants would spontaneously react effectively discharging the battery. Thus a separated cell is essential. A bipolar configuration would be a good design in this case because the reactants and products are all dissolved in the electrolyte and there are no changes in dimensions of the electrodes.

d) <u>production of adiponitrile</u>: the two reactions are

$$\mathrm{2CH_2CHCN + 2H^+ + 2e^- \rightarrow NC(CH_2)_4CN} \qquad (14\text{-}20)$$

$$\mathrm{H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^-}$$

Based on the reactions, an undivided cell is possible. Early commercial cells were membrane divided, but now undivided cells are used. These are much cheaper and easier to operate. A bipolar configuration is feasible.

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```
"!PROBLEM 14-15"
n=2
F=96485 [coulomb/mol]

eta_c=0.85

Vcell=2.0[V]

i=280 [A/m^2]

i*2*Ac=It; "A is the area of cells in parallel"

"Faraday's law"

m_dot=eta_c*(It/(n*F))*M
M=0.063546 [kg/mol]


Ac=1 [m^2]; "cell area"

h=0.045 [m]; "gap width"
w=0.030 [m]; "thickness of electrode"

Vol=Ac*(w+h)

cf2=3600 [s/hr]
Y=cf2*m_dot/Vol
```

SOLUTION

Unit Settings: SI C kPa J mass deg

Ac = 1 [m^2]	cf2 = 3600 [s/hr]
η_c = 0.85	F = 96485 [coulomb/mol]
h = 0.045 [m]	i = 280 [A/m^2]
It = 560 [A]	M = 0.06355 [kg/mol]
$\dot{m}$ = 0.0001567 [kg/s]	n = 2
Vcell = 2 [V]	Vol = 0.075 [m^3]
w = 0.03 [m]	Y = 7.524 [kg/h-m^3]

No unit problems were detected.

The extra anode is needed so that each cathode has an anode on both sides. The cathodes are plated on both sides.

The relative sizes of the electrodes will influence the current distribution and hence the uniformity of the resulting deposits. It may be useful to have the anode a bit smaller so that non-uniformity on the outside of the cathode would be reduced.

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```
"!PROBLEM 14-16"
n=2
no2=4
F=96485 [coulomb/mol]
p=1e5 [Pa]
R=8.314 [J/mol-K]
T=298 [K]

Ac=1 [m^2]; "cell area, one side"

L=2*W
Ac=L*W

i=3000 [A/m^2]


"Faraday's law"

"zinc"
mzn_dot=(i*2*Ac/(n*F))*Mzn
Mzn=0.063546 [kg/mol]; "molecular weight of Zn"

"oxygen"
mo_dot=(i*2*Ac/(no2*F))*Mo2
Mo2=0.016 [kg/mol]


"gas flow of oxygen"

p*V_dot=mo_dot*R*T/Mo2; "volumetric flowrate"
V_dot=h*W*V_s
h=0.02 [m]; "gap between electrodes"


Q=(4800/3600/100/200)  [m^3/s]
Q=h*W*V_e


c=100 [kg/m^3]

X=mzn_dot/(c*Q)

Re=rho*V_e*h/mu
rho=1000 [kg/m^3]
mu=0.001 [Pa-s]
```

SOLUTION

Unit Settings: SI C kPa J mass deg

$A_c = 1$ [m^2]	$c = 100$ [kg/m^3]
$F = 96485$ [coulomb/mol]	$h = 0.02$ [m]
$i = 3000$ [A/m^2]	$L = 1.414$ [m]
$Mo_2 = 0.016$ [kg/mol]	$\dot{m}_o = 0.0002487$ [kg/s]
$\mu = 0.001$ [Pa-s]	$M_{Zn} = 0.06355$ [kg/mol]
$\dot{m}_{Zn} = 0.001976$ [kg/s]	$n = 2$
$no_2 = 4$	$p = 100000$ [Pa]
$Q = 0.00006667$ [m^3/s]	$R = 8.314$ [J/mol-K]
$Re = 94.28$	$\rho = 1000$ [kg/m^3]
$T = 298$ [K]	$\dot{V} = 0.0003852$ [m^3/s]
$V_e = 0.004714$ [m/s]	$V_s = 0.02724$ [m/s]

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W = 0.7071 [m] X = 0.2964

No unit problems were detected.

In general, parallel flow from the bottom to the top of the tank would be preferred. In that situation, any gassing would help to facilitate the flow and provide mixing. However, such a flow pattern would tend to favor deposition at the bottom of the electrodes.

While bipolar stacks have advantages is several situations, such an arrangement would not be practical for zinc electrowinning since it would make it very difficult to strip and remove the product zinc. Also, such systems tend to form sludge in the bottom of the tank, which would be difficult to handle with a bipolar stack design.

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```
"!PROBLEM 14-17"
n=2
F=96485 [coulomb/mol]

pr=45000e3 [kg/yr]
cf1=(365*24*3600) [s/yr]
eta_c=0.85

Vs=180 [V]
Vcell=2.0[V]

i=300 [A/m^2]
mdot=eta_c*pr/cf1

It=40e3 [A]; "total series current"

i*A=It; "A is the area of cells in parallel"

"Faraday's law"

m_dot=(Ns*It/(n*F))*M
M=0.063546 [kg/mol]

Ns=Vs/Vcell

Ac=2 [m^2]; "cell area"

A=Ac*Np

DELTA_m=Ac*M*i*eta_c/(n*F)*t

t=(4*24*3600) [s]
```

SOLUTION

Unit Settings: SI C kPa J mass deg

$A = 133.3$ [m^2]	$A_c = 2$ [m^2]
cf1 = 3.154E+07 [s/yr]	$\Delta m = 58.04$ [kg]
$\eta_c = 0.85$	F = 96485 [coulomb/mol]
i = 300 [A/m^2]	It = 40000 [A]
M = 0.06355 [kg/mol]	mdot = 1.213 [kg/s]
$\dot{m} = 1.185$ [kg/s]	n = 2
Np = 66.67	Ns = 90
pr = 4.500E+07 [kg/yr]	t = 345600 [s]
Vcell = 2 [V]	Vs = 180 [V]

No unit problems were detected.

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"!PROBLEM 14-18"

ar=(1/0.03) [1/m]

Ac*100/V=ar

Ac=1.3 [m^2]

"V=2.4 [m^3]"

Vcell= 3 [V]

DH=439.7e3 [J/mol]

I=Ac*100*200*cd
cd=490 [A/m^2]

ri=I/n/F

n=2
F=96485 [coulomb/mol]

Q_dot-I*Vcell-ri*DH=0

rho=1000 [kg/m^3]

Qf=(4800/3600) [m^3/s]

Cp=4179 [J/kg-K]

rho*Qf*Cp*DT=Q_dot

SOLUTION

Unit Settings: SI C kPa J mass deg

Ac = 1.3 [m^2]
cd = 490 [A/m^2]
DH = 439700 [J/mol]
F = 96485 [coulomb/mol]
n = 2
$\dot{Q}$ = 6.725E+07 [J/s]
ri = 66.02 [mol/s]
Vcell = 3 [V]

ar = 33.33 [1/m]
Cp = 4179 [J/kg-K]
DT = 12.07 [K]
I = 1.274E+07 [A]
Qf = 1.333 [m^3/s]
ρ = 1000 [kg/m^3]
V = 3.9 [m^3]

No unit problems were detected.

An alternative to the carbon anode in the electrowinning of aluminum is the so-called inert anode. The cathode reaction is unchanged, but here, oxygen is evolved instead of consumption of carbon. Write the overall reaction, for the inert process. Compare the standard potential for the reaction with the reaction from equation 14-13. The Hall-Héroult process is already notoriously inefficient. What then are the possible advantages of the inert-anode process?

1) $2Al_2O_3 \rightarrow 4Al + 3O_2$
   $n = 12e^-$
   $U^{\theta}_{cell} = \dfrac{-\Delta G}{nF} = \dfrac{2(-1582.3)(1000)}{(12)(96485)}$
   $-2.73V$

2) $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$
   $n = 12e^-$
   $U^{\theta}_{cell} = \dfrac{-\Delta G}{nF} = \dfrac{-\big(3(-394.36) - 2(-1582.3)\big)(1000)}{(12)(96485)}$
   $= -1.71V$

As the equilibrium potential is significantly higher, energy costs would increase. Possible advantages include:

1) Would no longer have the cost of consumable carbon electrodes and the associated costs of replacement.
2) Would not produce carbon dioxide as a byproduct.
3) It may be possible to collect the O_2 as a product, but you would probably want to pressurize the cell if that were the case. There would be additional costs associated with collection and distribution that may prohibit this possibility on the basis of economics.

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```
"!PROBLEM 14-20"
kappa=25 [1/ohm-m]
epsilon=0.45
Q=20 [m^3/h]
dp=0.002 [m]
D=0.7e-9 [m^2/s]
Ac=0.75 [m^2]
c1=4
c2=0.05
n=2
F=96485 [coulomb/mol]
M_Hg=0.20059 [kg/mol]
M_o=0.018 [kg/mol]

vs=(Q/cf1)/Ac
vx=vs/epsilon

cf1=3600 [s/hr]

p1=100 [kPa]
T1=25 [C]

rho=density(water, t=t1, p=p1)
mu=viscosity(water, t=t1, p=p1)

Re=vs*dp*rho/mu
Sc=mu/rho/D

"kc*dp/D=0.83*Re^0.56*Sc^0.33333"; "Pickett"
"(kc/vs)*Sc^0.667=0.010/epsilon+(0.863/epsilon)/(Re^0.58-0.483)"; "Gupta and Thodos"
"kc/vs=1.17*Re^(-0.415)*Sc^(-0.667)"; "Sherwood"
(kc/vs)*Sc^0.667=(1.09/epsilon)*Re^(-0.667); "Wilson and Geankoplis"


a=6*(1-epsilon)/dp

L=(vs/(a*kc))*ln(c1/c2)

c_in=(c1/1e6)*rho/M_Hg
c_out=(c2/1e6)*rho/M_Hg

DELTAphi=(n*F*vs*vs/(kappa*kc*a))*(c_in-c_out-(kc*a/vs)*L*c_out)
```

SOLUTION

Unit Settings: SI C kPa J mass deg

$a = 1650$ [1/m]
$Ac = 0.75$ [m^2]
$c1 = 4$
$c2 = 0.05$
$cf1 = 3600$ [s/hr]
$c_{in} = 0.01988$ [mol/m^3]
$c_{out} = 0.0002485$ [mol/m^3]
$D = 7.000E-10$ [m^2/s]
$\Delta\phi = 0.2037$ [V]
$dp = 0.002$ [m]
$\varepsilon = 0.45$
$F = 96485$ [coulomb/mol]
$\kappa = 25$ [$1/\Omega$-m]
$kc = 0.00002337$ [m/s]

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$L = 0.8417$ [m]
$\mu = 0.0008905$ [Pa-s]
$M_{Hg} = 0.2006$ [kg/mol]
$M_o = 0.018$ [kg/mol]
$n = 2$
$p1 = 100$ [kPa]
$Q = 20$ [m^3/h]
$Re = 16.59$
$\rho = 997.1$ [kg/m^3]
$Sc = 1276$
$T1 = 25$ [C]
$vs = 0.007407$ [m/s]
$vx = 0.01646$ [m/s]

No unit problems were detected.

Problem statement:

Consider the waste-water cleanup with porous electrodes shown in illustration 14-14. If the particle size were increased to 2 mm, to what value would the effective conductivity need to be increased in order to keep the Hg within the limits. Use an area of 0.75 m^2.

Effective Conductivity:

$$\Delta\phi = \frac{nF\mathrm{v}_s^2}{\kappa_{eff}k_c a}(C_{Hg,in} - C_{Hg,out} - \frac{k_c a}{\mathrm{v}_s}Lc_{Hg,out})$$

$$\Rightarrow \kappa_{eff} = \frac{(2)(96485)(0.007407)^2}{(0.2)(2.337\times10^{-5})(1650)}(0.01988 - 0.0002485 -$$

$$\frac{(2.337\times10^{-5})(1650)}{0.007407}(0.8417)(0.0002485)$$

$$\kappa_{eff} = 26.8\frac{S}{m}$$

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PROBLEM 14-21

$cf1 = 365 \cdot 24 \cdot 3600$ [s/yr]

$cf2 = 3.6 \times 10^{6}$ [J/kW-h]

$F = 96485$ [coulomb/mol]

$M = 0.006941$ [kg/mol]

$n = 1$

$\eta_f = 0.95$

$U = 3.6$ [V]

$se = I \cdot V \cdot \frac{cf1}{cf2 \cdot pr}$ *specificy energy kW-h/kg*

$\eta_e = \eta_f \cdot \frac{U}{V}$

$se = 35$ [kW-h/kg]

$\eta_f \cdot \frac{pr}{cf1} = M \cdot \frac{I}{n \cdot F}$

$pr = 1$ [kg/yr]

SOLUTION

Unit Settings: SI C kPa J mass deg

$cf1 = 3.154E+07$ [s/yr]
$cf2 = 3.600E+06$ [J/kW-h]
$\eta_e = 0.3584$
$\eta_f = 0.95$
$F = 96485$ [coulomb/mol]
$I = 0.4187$ [A]
$M = 0.006941$ [kg/mol]
$n = 1$
$pr = 1$ [kg/yr]
$se = 35$ [kW-h/kg]
$U = 3.6$ [V]
$V = 9.541$ [V]

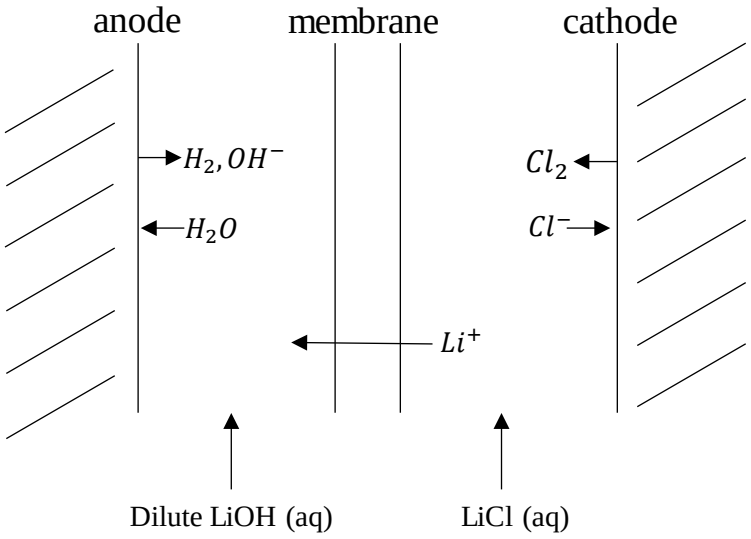
No unit problems were detected.

The growth in the lithium-ion battery market has raised demand for lithium. Rechargeable batteries typically use lithiated metal oxides, and the precursor is LiOH not lithium metal. Describe a method to produce LiOH by a process similar to that used for caustic soda using an ion-exchange membrane.

Looking for a process like the chlor alkali process that produces $LiOH$ as a product.

Assume 1) input = aqueous solution of LiCl

2) Membrane cell with cation exchange membrane



Reactions: $2Cl^- \rightarrow Cl_2 + 2e^-$ (anode)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (cathode)

Current is carried across the membrane by Li^+ ions

Products: $Cl_2, H_2, LiOH$

Would need to evaporate off liquid to produce LiOH salt.

U_{cell} is essentially the same, except for the result of any activity differences due to Li^+ instead of Na^+

U_{cell} will also be affected by differences in $\Delta\phi$ across the membrane during operation.

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"!PROBLEM 14-23"

pr=1e8 [kg/yr]

cf1=365*24*3600 [s/yr]
F=96485 [coulomb/mol]
M=0.10814 [kg/mol]
n=2

m_dot=pr/cf1

eta_c=0.95

P=I*V
V=4.6 [V]

eta_c*m_dot=M*I/(n*F)

SOLUTION
Unit Settings: SI C kPa J mass deg

cf1 = 3.154E+07 [s/yr]
F = 96485 [coulomb/mol]
M = 0.1081 [kg/mol]
n = 2
pr = 1.000E+08 [kg/yr]

η_c = 0.95
I = 5.376E+06 [A]
$\dot{m}$ = 3.171 [kg/s]
P = 2.473E+07 [W]
V = 4.6 [V]

No unit problems were detected.

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"!PROBLEM 14-24"

pr=2e8 [kg/yr]

cf1=365*24*3600 [s/yr]
cf2=3600000 [J/kW-h]
F=96485 [coulomb/mol]
M=0.10814 [kg/mol]
n=2

m_dot=pr/cf1

P=54e6 [W]

eta_c=0.90

P=I*V

eta_c*m_dot=M*I/(n*F)

se=p*cf1/cf2/pr; "specificy energy kW-h/kg"

U=3.08 [V]

eta_e=eta_c*U/V

SOLUTION
Unit Settings: SI C kPa J mass deg

cf1 = 3.154E+07 [s/yr]	cf2 = 3.600E+06 [J/kW-h]
η^c = 0.9	η^e = 0.5228
F = 96485 [coulomb/mol]	I = 1.019E+07 [A]
M = 0.1081 [kg/mol]	$\dot{m}$ = 6.342 [kg/s]
n = 2	P = 5.400E+07 [W]
pr = 2.000E+08 [kg/yr]	se = 2.365 [kW-h/kg]
U = 3.08 [V]	V = 5.302 [V]

No unit problems were detected.

To avoid hydrogen evolution, use a solvent other than water with a wider stability window.

Note that for some systems with a high hydrogen overpotential will suffice (e.g., lead).

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"!PROBLEM 14-25"

```
T=353 [K]
F=96485 [coulomb/mol]
R=8.314 [J/mol-K]
cf1=3600 [s/h]
n=2


Vcell=2.25 [V]
Ac=1 [m^2]

P=1e5 [W]
U=1.18 [V]

i=3000 [A/m^2]
eta_c=0.985

It=i*Ac; "current in stack"
P=It*Vcell*Ns; "used to determine number of cells connected in series in the stack"

p_n=1.0e5 [Pa]
T_n=273 [K]

N_H2=eta_c*It*Ns/(n*F)

p_n*V_n=N_H2*R*T_n

V_h=V_n*cf1

se=P/V_h



eta_e=eta_c*U/Vcell

eta_hhv=hhv/se
hhv=3540 [W-h/m^3]
```

SOLUTION

Unit Settings: SI C kPa J mass deg

$Ac = 1$ [m^2]	$cf1 = 3600$ [s/h]
$\eta_c = 0.985$	$\eta_e = 0.5166$
$\eta_{hhv} = 0.6562$	$F = 96485$ [coulomb/mol]
$hhv = 3540$ [$W\text{-}h/m^3$]	$i = 3000$ [A/m^2]
$It = 3000$ [A]	$n = 2$
$Ns = 14.81$	$N_{H2} = 0.2269$ [mol/s]
$P = 100000$ [W]	$p_n = 100000$ [Pa]
$R = 8.314$ [J/mol-K]	$se = 5395$ [$W\text{-}h/m^3$]
$T = 353$ [K]	$T_n = 273$ [K]
$U = 1.18$ [V]	$Vcell = 2.25$ [V]
$V_h = 18.54$ [m^3/h]	$V_n = 0.005149$ [m^3/s]

No unit problems were detected.

Electrolyzers and fuel cells are envisioned to be a part of an energy storage system for the electrical grid. When supply exceeds demand, hydrogen is generated and stored. When demand exceeds supply, this stored hydrogen is used in a fuel cell to generate electricity. Using the efficiency for electrolysis from illustration 14-13 and assuming a fuel-cell system efficiency of 60 %, what is the round-trip efficiency?

Looking for round trip efficiency

$$\frac{Electrical\ Energy\ Out\ (discharge)}{Electrical\ Energy\ In\ (charge)}$$

From Illustration 14.13: 63% of energy supplied is used to produce H_2

If we begin by supplying an arbitrary amount of energy

Energy in $= 100$

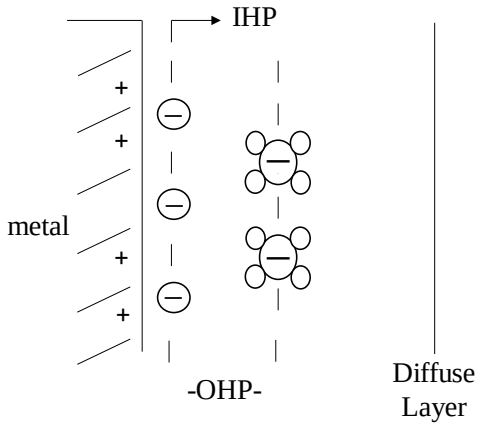
Maximum Energy Available $= 63$ (rest lost in H_2 evolution)

Fraction out $= (0.60)63 = 37.8$

This is the amount from our original 100 that is available.

$\therefore \boldsymbol{Round\ trip\ efficiency = 37.8\%}$

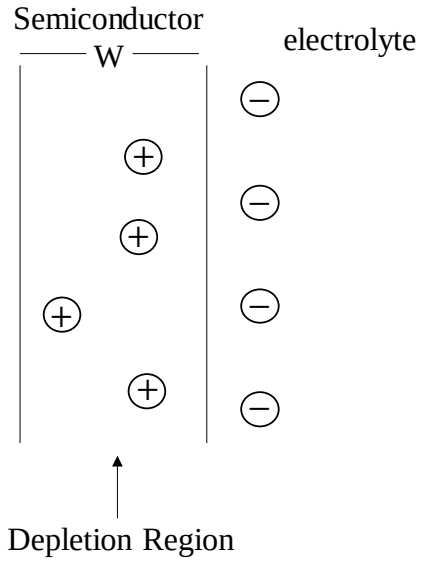
Sketch the interface between a metal and electrolyte. Assume that the metal electrode has a small positive charge. Identify the inner and outer Helmholtz plane and the diffuse layer. What determines the thickness of the diffuse layer? Make a similar sketch for the semiconductor/electrolyte interface for an *n*-type semiconductor and identify the depletion region and the Helmholtz plane. What determines the thickness of the depletion region?



positive charge at surface of the metal

The Debye length is determined by the number of charge carriers in the electrolyte.

$$\lambda = \sqrt{\frac{\varepsilon RT}{F^2 \sum z_i^2 c_{i,b}}} \sim 1nm$$



W much greater than λ

$$W = \sqrt{\frac{2\varepsilon(\eta - V_{fb})}{qN_D}}$$

Dopant Concentration

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Problem 15-02

$k = 1.3806 \times 10^{-23}$ [J/K]

$q = 1.6022 \times 10^{-19}$ [coulomb]

$cf1 = 1.6022 \times 10^{-19}$ [J/eV]

$T = 298$ [K]

a

$$Et = k \cdot \frac{T}{cf1}$$

$Eg = 1.1$ [eV]

$$Eg = k \cdot \frac{T_{Si}}{cf1}$$

Because the band gap is so much larger than the thermal energy (kT) only an extremely small fraction of the electrons will have sufficient energy to be excited into the conduction band.

SOLUTION

Unit Settings: SI C kPa kJ mass deg

cf1 = 1.602E-19 [J/eV]
Et = 0.02568 [eV]
q = 1.602E-19 [coulomb]
T_{Si} = 12766 [K]

Eg = 1.1 [eV]
k = 1.381E-23 [J/K]
T = 298 [K]

No unit problems were detected.

Determine the doping (in ppb) of phosphorous or arsenic that must be added to silicon to achieve a concentration of 10^{15} cm^{-3}. The density of silicon is 2329 kg/m^3. Would this doping create an *n*- or *p*-type semiconductor? What would be its resistivity?

For low doping levels

$$ppb \approx \frac{mass\ of\ dopant}{mass\ of\ silicon} \times 10^9$$

$$= \frac{C\ MW}{\rho N_{AV}}$$

$$C = 10^{15} cm^{-3}$$

$$Density\ of\ Silicon = 2329 \frac{kg}{m^3}$$

P: 30.97 $\frac{g}{mol}$ As: 74.92 $\frac{g}{mol}$

$ppb = 22.1$ $ppb = 53.4$

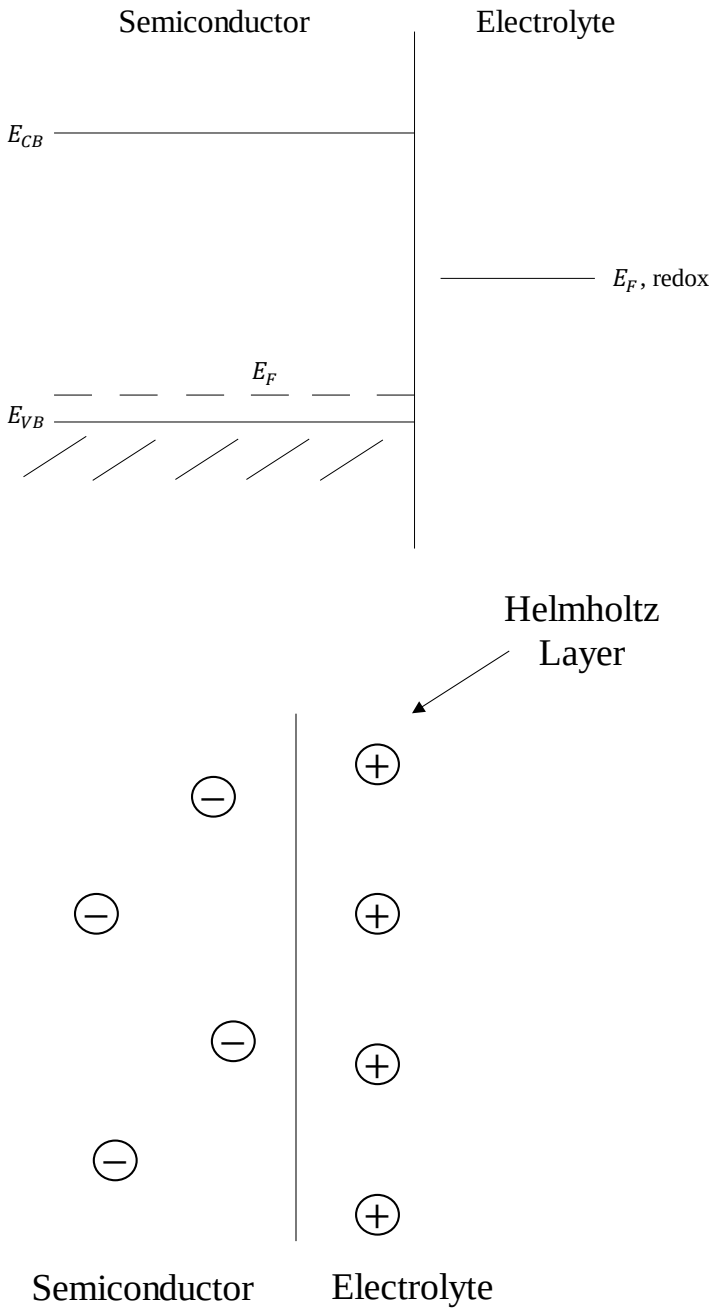
Both P and As have five valence electrons
$\Longrightarrow$ n-type semiconductors

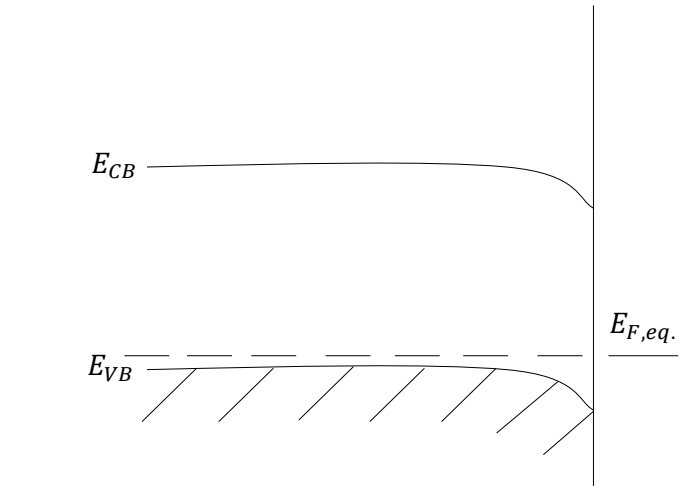
N_D is the same for both dopants. From Fig 15.8,

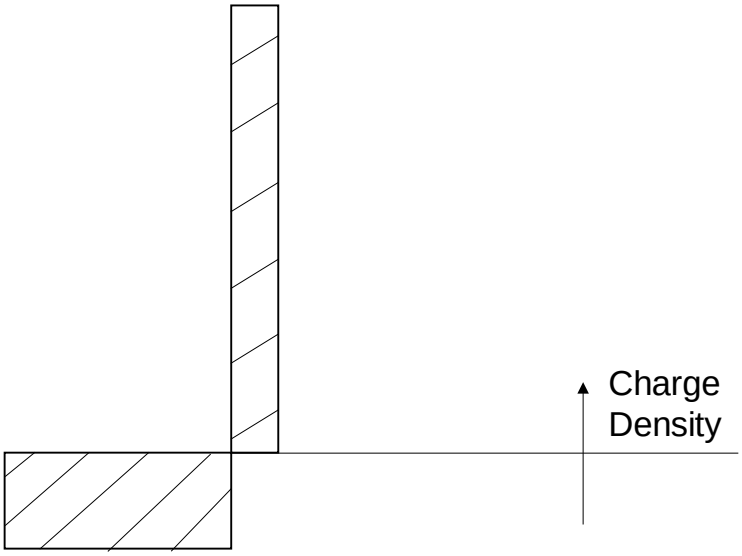
$$\rho_P = \sim 4.6 \text{ ohm-cm} = \rho_{As}$$

Analogous to Figure 15-10, sketch the charge distribution and band bending for a *p*-type semiconductor brought into contact with an electrolyte. Assume that before equilibration the Fermi level of the redox couple is in the middle of the conduction and valence bands.

p-type Semiconductor:




E_{CB}
$E_{F,eq.}$
E_{VB}


Charge
Density

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Problem 15.5, n type semiconductor

$m = 7.91 \times 10^{7}$ [$m^4/(Farad^2\text{-}V)$]

$b = 8.635 \times 10^{7}$ [$m^4/(Farad^{2)}$]

$yf = m \cdot \eta + b$

use x intercept from fit to get flat band potential

$q = 1.6022177 \times 10^{-19}$ [coulomb]

Nd=3e21 [$1/m^3$]

$eo = 8.854188 \times 10^{-12}$ [farad/m]

$er = 11.9$

$yf = 0$

$\eta = V_{fb}$

use slope to get doping level

$$m = \frac{2}{er \cdot eo \cdot q \cdot Nd}$$

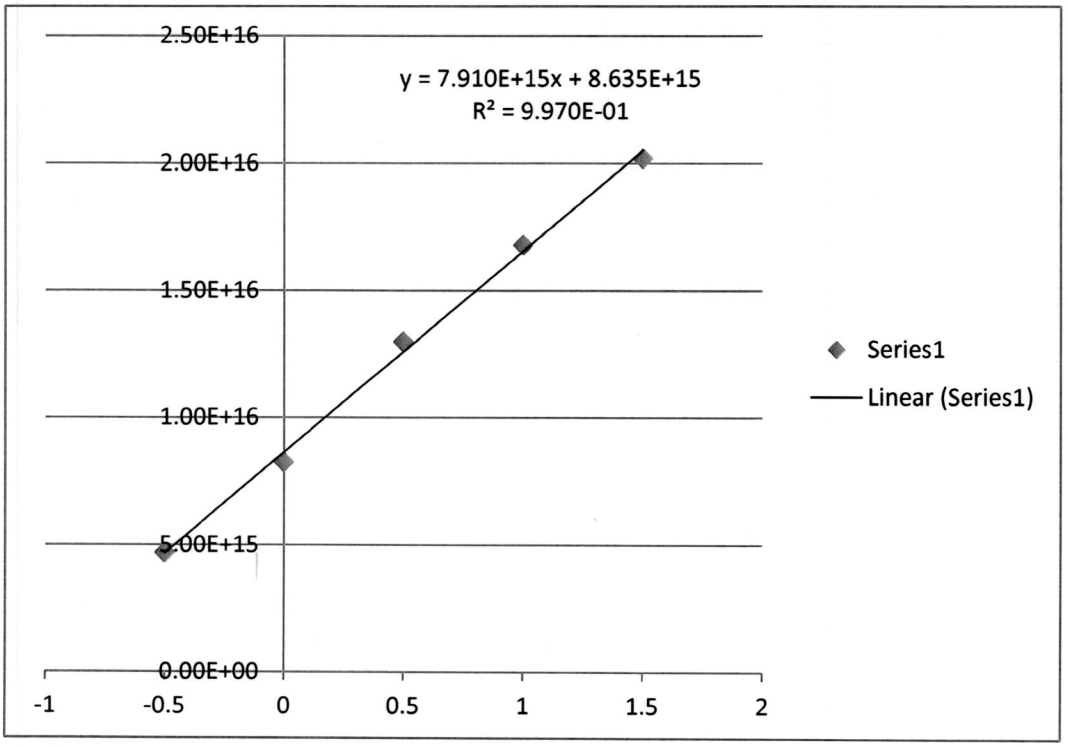
SOLUTION

Unit Settings: SI C kPa kJ mass deg

b = 8.635E+07 [$m^4/(Farad^2)$]
eo = 8.854E-12 [farad/m]
er = 11.9
η = -1.092 [V]
m = 7.910E+07 [$m^4/(Farad^2\text{-}V)$]
Nd = 1.498E+21 [$1/m^3$]
q = 1.602E-19 [coulomb]
V_{fb} = -1.092 [V]
yf = 0 [$m^4/farad^2$]

No unit problems were detected.

potential, V	1/c^2	C, F/cm^2
-0.5	4.70E+15	1.459E-08
0	8.25E+15	1.101E-08
0.5	1.30E+16	8.771E-09
1	1.68E+16	7.715E-09
1.5	2.02E+16	7.036E-09



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Problem 15.6, p-type

$m = -3.63 \times 10^{7}$ [$m^4/(Farad^2\text{-}V)$]

$b = -1.29 \times 10^{7}$ [$m^4/(Farad^{2)}$]

$yf = m \cdot \eta + b$

use x intercept from fit to get flat band potential

$q = 1.6022177 \times 10^{-19}$ [coulomb]

$eo = 8.854188 \times 10^{-12}$ [farad/m]

$er = 11.9$

$yf = 0$

$\eta = V_{fb}$

use slope to get doping level

$$m = \frac{-2}{er \cdot eo \cdot q \cdot Nd}$$

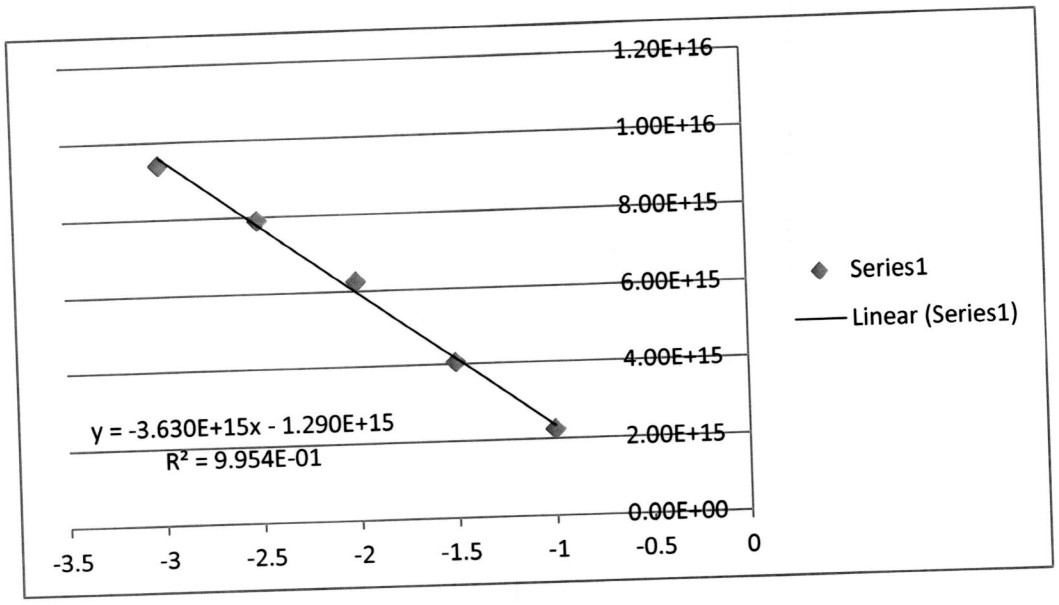
SOLUTION

Unit Settings: SI C kPa kJ mass deg

b = -1.290E+07 [$m^4/(Farad^2)$]
eo = 8.854E-12 [farad/m]
er = 11.9
η = -0.3554 [V]
m = -3.630E+07 [$m^4/(Farad^2\text{-}V)$]
Nd = 3.264E+21 [$1/m^3$]
q = 1.602E-19 [coulomb]
V_{fb} = -0.3554 [V]
yf = 0 [$m^4/farad^2$]

No unit problems were detected.

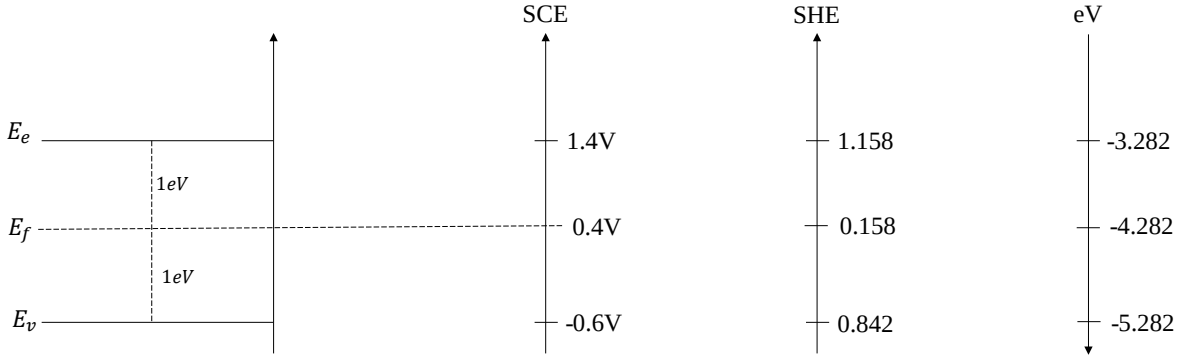
potential, V	1/c^2	C, F/cm^2
-1	2.25E+15	2.108E-08
-1.5	4.05E+15	1.571E-08
-2	6.25E+15	1.265E-08
-2.5	7.90E+15	1.125E-08
-3	9.40E+15	1.031E-08



An intrinsic semiconductor has a 2 eV band gap. If the Fermi level of the electrode corresponds to 0.4 V relative to a SCE reference, sketch the energy levels and show the corresponding energies in eV of the band edges using a vacuum scale.

Band gap is $2eV$, intrinsic semiconductor

$\Longrightarrow$ Fermi-level is between E_c and E_V



To convert SCE potential to SHE, we need to know that SCE is 0.242V positive of SHE.

Therefore, need to subtract 0.242V. Subtract 4.44 to get to eV vacuum

SCE	SHE	eV
1.4	1.158	-3.282
0.4	0.158	-4.282
-0.6	-0.842	-5.282

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problem 15-8, strength of electric field

$Nd = 1 \times 10^{22}$ [m^{-3}]

$\varepsilon_o = 8.854188 \times 10^{-12}$ [farad/m]

$er = 12$

$\varepsilon = \varepsilon_o \cdot er$

$W = 1.0 \times 10^{-7}$ [m]

$q = 1.602177 \times 10^{-19}$ [coulomb]

$$Field = q \cdot Nd \cdot \frac{W}{\varepsilon}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

ε = 1.063E-10 [farad/m]
ε_o = 8.854E-12 [farad/m]
er = 12
Field = 1.508E+06 [V/m]
Nd = 1.000E+22 [m^{-3}]
q = 1.602E-19 [coulomb]
W = 1.000E-07 [m]

No unit problems were detected.

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Problem 15-09

$cf1 = 1000000$ [cm^3/m^3]

$cf2 = 6.022 \times 10^{23}$ [1/mol]

0.1 M salt

$c = 1000$ [mol/m^3]

$$c_{cc} = 2 \cdot c \cdot \frac{cf2}{cf1}$$

the concentration of charge carriers is at least three orders of magnitude higher in the electrolyte.

SOLUTION

Unit Settings: SI C kPa kJ mass deg

c = 1000 [mol/m^3]
cf1 = 1000000 [cm^3/m^3]
cf2 = 6.022E+23 [1/mol]
c_{cc} = 1.204E+21 [$1/cm^3$]

No unit problems were detected.

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Problem 15-10

R = 8.314 [J/mol-K]

T = 298 [K]

F = 96485 [coulomb/mol]

MW=0.32924 [kg/mol]

m=10e-6 [kg]

V=100e-6 [m^3]

*c_K=3*m/MW/V*

c_{ferri}=c_{ferro}
*c_{ferro}=0.5*m/MW/V*

I=c_K+c_{ferri}+c_{ferro}

*lambda=sqrt(epsilon*epsilon$_{r}$*R*T/F/F/I)*

$\varepsilon = 8.854 \times 10^{-12}$ [$m^{-3}\cdot kg^{-1}\cdot s^4\cdot A^2$]

$\varepsilon_r = 78$

c=100 [mol/m^3]

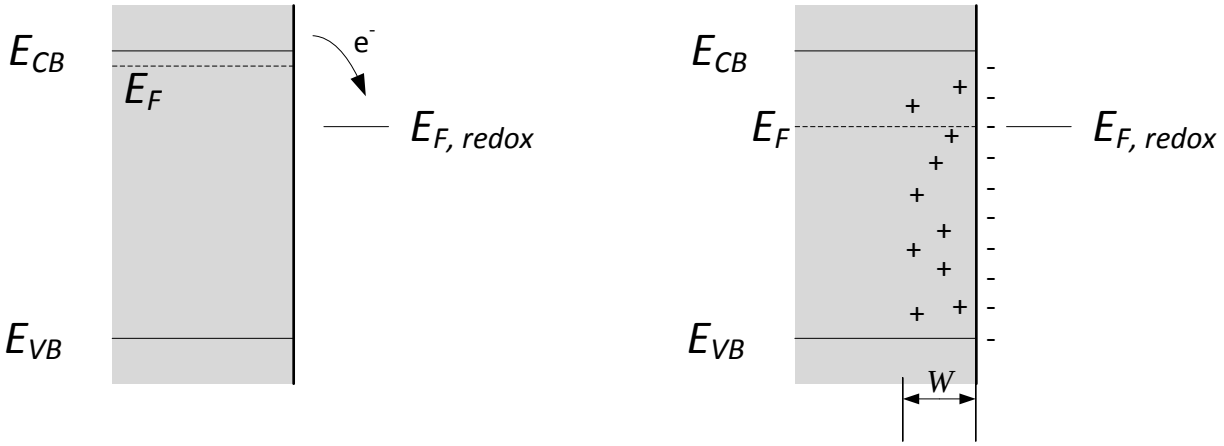
$\lambda_n = 4.2 \times 10^{-7}$ [m] *thickness of depletion region from Illustration 15-3*

$I_n = 2 \cdot c$

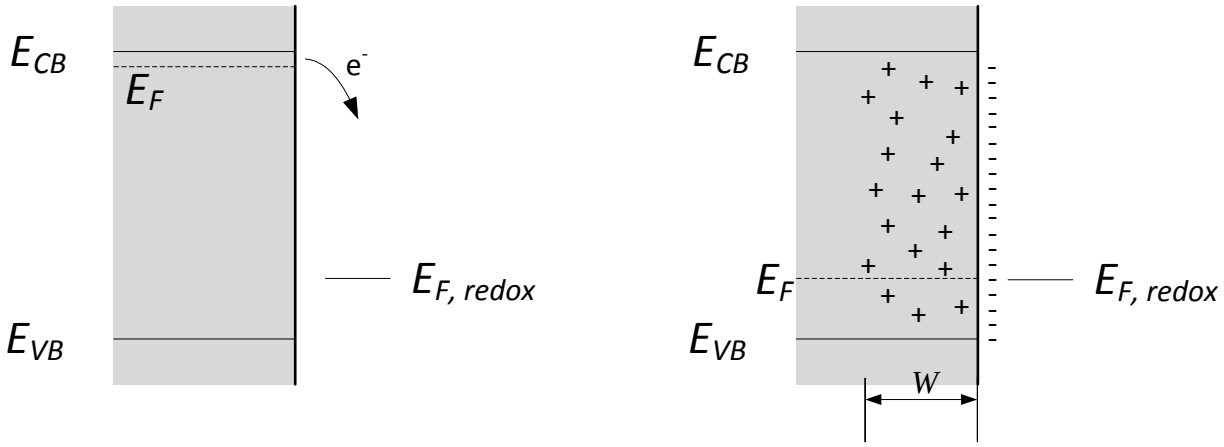
$$\lambda_n = \sqrt{\varepsilon \cdot \varepsilon_r \cdot R \cdot \frac{T}{F \cdot F \cdot I_n}}$$

SOLUTION
Unit Settings: SI C kPa kJ mass deg
c = 0.000521 [mol/m^3]
ε = 8.854E-12 [$m^{-3}\cdot kg^{-1}\cdot s^4\cdot A^2$]
ε_r = 78
F = 96485 [coulomb/mol]
I_n = 0.001042 [mol/m^3]
λ_n = 4.200E-07 [m]
R = 8.314 [J/mol-K]
T = 298 [K]

No unit problems were detected.



In both cases, electrons will be transferred from the semiconductor to the electrolyte until the fermi levels are the same. In the second case, the fermi level of the redox couple is much lower than the initial fermi level in the semiconductor. As a result, more charge is transferred. Thus, the depletion region has more charge and it is thicker.



Starting with equation 15-17 (Beer-Lambert Law), show that the penetration depth (distance at which the intensity of light is reduced by a factor of 1/e) is inversely proportional to the absorption coefficient. Using equation 15-20, determine the penetration depth in crystalline silicon for light with wavelengths of 400, 600, and 1000 nm

$$\frac{dI''}{dx} = -\alpha I''$$

$$\int_{I_o''}^{I''} \frac{dI''}{I''} = -\int_{o}^{\delta} \alpha dx$$

$$ln\frac{I''}{I_o''} = -\alpha\delta$$

$$\frac{I''}{I_o''} = exp^{-\alpha\delta}$$

$$\frac{1}{e} = exp^{-\alpha\delta}$$

$$\delta = \frac{1}{\alpha}$$

$\lambda\ (nm)$	E (ev)	$\alpha(cm^{-1})$	$\delta(\mu m)$
400	3.1	76229	0.13
600	2.07	3919	2.55
1000	1.24	57.4	174

15-13. Describe three methods of generating mobile charge carriers in semiconductors.

Thermal excitation of electrons, kT. Electrons from the valence band reach the conduction band due to ambient thermal excitation. As a result, two charge carriers are created: an electron in the conduction band and a hole in the valence band. At typical temperatures, the band gap is large enough that very few electrons are in the conduction band. As a result, the intrinsic conductivity of the semiconductor is low, and intrinsic semiconductors are essentially insulators.

Photo-excitation of electrons, $h\nu$. This process is similar to thermal excitation, but the energy comes from a photon. As before a mobile electron and hole are created in their respective bands.

Doping, small amounts of elements with either an excess or shortage of valence electrons are substituted into the crystal lattice. These trace impurities create either holes or excess electrons. You can also get the same effect with nonstoichiometric semiconductors, such as CdTe, which does not require doping.

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problem 15-14

$cf1 = 1.6 \times 10^{-19}$ [J/eV]

$cf2 = 1.24$ [μm-eV] *equation 15-15*

$cf3 = 1000$ [nm/μm]

$cf4 = 1$ [1/cm]

$\Delta = 0.1$ [eV]

fraction absorbed set at 0.95, use equation 15-18 to get W

$0.95 = 1 - \mathbf{exp}\left[-\alpha_s \cdot Ws\right]$ *for silicon*

$E_{gs} = 1.15$ [eV]

$$\lambda_s = \frac{cf2}{E_{gs} + \Delta}$$

$\lambda_{sf} = cf3 \cdot \lambda_s$ *converts to nanometers*

equation 15-20 fits data for silicon

$A = -5.7536 \times 10^{-8}$ [1/(nm)^3]

$B = 0.00012221$ [1/(nm)^2]

$C = -0.093322$ [1/nm]

$D = 32.6999$

$$\mathbf{ln}\left[aa\right] = A \cdot \lambda_{sf}^{\ 3} + B \cdot \lambda_{sf}^{\ 2} + C \cdot \lambda_{sf}^{\ 1} + D$$

$\alpha_s = aa \cdot cf4$

repeat for GaAs

$0.95 = 1 - \mathbf{exp}\left[-\alpha_g \cdot Wg\right]$ *for GaAS*

$\alpha_g = 5000$ [1/cm] *from figure 15-17*

SOLUTION

Unit Settings: SI C kPa kJ mass deg

A = -5.754E-08 [1/(nm)^3]
α_g = 5000 [1/cm]
B = 0.0001222 [1/(nm)^2]
cf1 = 1.600E-19 [J/eV]
cf3 = 1000 [nm/μm]
D = 32.7
E_{gs} = 1.15 [eV]
aa = 68.09
α_s = 68.09 [1/cm]
C = -0.09332 [1/nm]
cf2 = 1.24 [μm-eV]
cf4 = 1 [1/cm]
Δ = 0.1 [eV]
λ_s = 0.992 [μm]

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λ_{sf} = 992 [nm]
Ws = 0.044 [cm]
Wg = 0.0005991 [cm]

No unit problems were detected.

Parameter	Description	Intrinsic or design parameter	Implications
Band gap, E_g	Difference in energy, usually expressed in [eV] between the conduction and valence bands. Most important property of semiconductor.	Intrinsic: Every solid has its own band structure. Gap depends on material chosen. Band gaps decrease with increasing temperature. Very high doping densities can cause the band gap to shrink	Selection of material is particularly important for photo-electrochemistry because photon must have at least enough energy to excite an electron to the conduction band.
Fermi level, E_F	Energy level expressed in [eV]. Two equivalent descriptions: probabilistic, hypothetical energy level at which it is equally probable that the energy level is occupied by an electron or vacant; thermodynamically it is the electrochemical potential of an electron	Design: the Fermi level is changed by doping and by altering the potential of the electrode.	At equilibrium the Fermi level of the redox couple is equal to that in the semiconductor.
Flat band potential, V_{fb}	The potential of a semiconductor electrode measured with respect to a specific reference electrode when there is no "band bending" or said another way there is no charge in the depletion layer and its thickness is zero	Design: depends on entire electrolyte, semiconductor system, namely redox couple, doping levels, reference electrode	Important parameter for photoelectrochemical systems.
Doping levels, N_A ,N_D	Amount of impurity added to the semiconductors. Can be either acceptor or donor atoms to create *p* or *n*-type semiconductors. Concentration expressed in ppb or cm^{-3}	Design: these acceptor and donor and purposely added to achieve design goals.	Acceptor or donor selected to create either *n* or *p* type. Levels chosen to achieve desired conductivity and width of the depletion layer.
Absorption coefficient, α	proportionality constant that relates change in light intensity with distance, units are [m^{-1}]	Intrinsic: physical property of the material,	Energy of photon must be above band gap and absorption must occur in or near the depletion zone. Absorption in semiconductors can either be direct or indirect.
Width of depletion layer, W	distance over which charge separation occurs in the semiconductor, also called the space charge region. Expressed in [m].	Design: Altered by the doping and the potential of the semiconductor electrode.	Vital for charge separation of photo-generated charge carriers. Without this space charge layer, electrons and holes would recombine.

Most of the solar energy is in the visible spectrum, 400-700 nm. Equation 15-15 can be used to relate these wavelengths band gap energies.

400 nm	0.4 μm	3.1 eV
700 nm	0.7 nm	1.77 eV

These values are then compared with the band gaps of the materials from Figure 15-9

Si	1.1 eV
GaAs	1.4 eV
CdTe	1.5 eV
TiO_2	3.2 eV

We see that the band gap for TiO_2 is too large for this to be effective in directly converting solar energy to electricity—there is insufficient energy in the photons to excite electrons to the conduction band. The band gaps for the other semiconductors are below the energy of the majority of photons. Threshold in the near-IR region are the most efficient, these include materials with band gaps of 1.1-1.7 eV such as Si, GaAs, and CdTe. However, any energy much above the band gap is mostly wasted as the electrons are quickly thermalized to the energy of the conduction band edge. For these reasons, Si is the best choice.

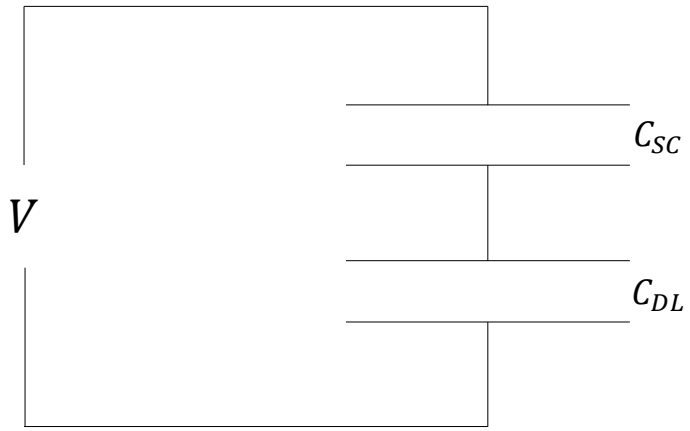
In principle, any material with a band gap greater than 1.229 eV (U^0=1.229 V) could be used for hydrogen production. In practice, more than 2.0 eV are needed. What's more the materials with small band gaps are typically not stable and will corrode or passivate. TiO_2 has a large band gap and is stable.

In section 15.3 it is stated that "the potential drop across the Helmholtz double layer will be much less than that across the depletion layer of the semiconductor." Given how capacitors in series behave, justify this claim. Remember that the capacitance of the double layer is much higher than that of the depletion region in a semiconductor.

For a capacitor: $C = \frac{Q}{V}$

$$\Longrightarrow V = \frac{Q}{C} \qquad Q = CV$$

For capacitors in series, Q is the same.



$$\frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_{DL}}$$

$$V_{DL} = \frac{Q}{C_{DL}} \qquad V_{sc} = \frac{Q}{C_{sc}}$$

Since Q is the same, if $C_{DL} \gg C_{sc}$ then the potential across the double layer is much smaller than the potential drop in the space charge layer.

In section 15-4 a simplified version of the Mott-Schottky equation was developed for an *n*-type semiconductor (see equation 15-8). What is the analogous expression for a *p*-type semiconductor? For what range of overpotentials does it apply? Why?

$$\frac{1}{C^2} = \frac{-2(\eta - V_{fb})}{\varepsilon A^2 q N_A}$$

$$\frac{d^2\phi}{dx^2} = \frac{-\rho_e}{\varepsilon} \approx \frac{qN_A}{\varepsilon}$$

$$\frac{d\phi}{dx} = \frac{qN_A x}{\varepsilon} + constant$$

$$at\ x = W, \frac{d\phi}{dx} = 0$$

$$\frac{d\phi}{dx} = \frac{q_A N_A (x - W)}{\varepsilon}$$

$$\int_{\phi_{int}}^{\phi} d\phi = \frac{q_A N_A}{\varepsilon} \int_o^w (x - W) dx$$

$$V_{SC} = \phi - \phi_{int} = \frac{q_A N_A}{\varepsilon} \left[\frac{x^2}{2} - Wx \right]_o^W$$

$$\frac{q_A N_A}{\varepsilon} \left[\frac{W^2}{2} - W^2 \right] = \frac{-q_A N_A}{\varepsilon} \frac{W^2}{2}$$

$\phi_{int} = \phi + \frac{q_A N_A W^2}{2\varepsilon}$ (interface positive relative to bulk)

$$V_{int} = V_{bulk} + \frac{q_A N_A W^2}{2\varepsilon}$$

$$\eta = V - U$$

$$(V - U) - (V_{int} - U) = -\frac{q_A N_A W^2}{2\varepsilon}$$

$$\eta + (U - V_{int}) = -\frac{q_A N_A W^2}{2\varepsilon}$$

$$V_{SC} = V - V_{int} = -\frac{qN_A W^2}{2\varepsilon}$$

$$\eta + V_{SC,eq} = \eta - V_{fb}$$

$$V_{fb} - \eta = \frac{qN_A W^2}{2\varepsilon}$$

$$W = \sqrt{\frac{2\varepsilon\left(V_{fb} - \eta\right)}{qN_A}} \qquad for\ V_{fb} > \eta$$

$$Q_{SC} = qN_A W = \sqrt{2\varepsilon q N_A (V_{fb} - \eta)}$$

$$C = A\frac{dQ_{SC}}{dV} = \sqrt{2\varepsilon q N_A}\ \frac{d(V_{fb} - \eta)^{1/2}}{d\eta}$$

$$= -A\sqrt{2\varepsilon q N_A}\frac{1}{2}\left(V_{fb} - \eta\right)^{-\frac{1}{2}}$$

$$\frac{1}{C^2} = \frac{4(\eta - V_{fb})}{A^2 2\varepsilon q N_A}$$

$$\boxed{\frac{1}{C^2} = \frac{-2(\eta - V_{fb})}{A^2 \varepsilon q N_A}}$$

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problem 15-19

$\Phi = 0.9$

Lp=200e-6 [m]

$\alpha = 100000$ [1/m]

$$\Phi = 1 - \left[\frac{\exp(-\alpha \cdot W)}{1 + \alpha \cdot Lp}\right]$$

calculation of W

$\eta = -0.1$ [V]

$V_{fb} = -0.4$ [V]

$q = 1.602 \times 10^{-19}$ [coulomb]

$N_D = 3 \times 10^{21}$ [1/m^3]

$er = 11.9$

$\varepsilon = 8.854 \times 10^{-12}$ [coulomb/(V-m)]

$$W = \sqrt{2 \cdot er \cdot \varepsilon \cdot \left[\frac{\eta - V_{fb}}{q \cdot N_D}\right]}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

α = 100000 [1/m]
ε = 8.854E-12 [coulomb/(V-m)]
er = 11.9
η = -0.1 [V]
Lp = 0.00008644 [m]
N_D = 3.000E+21 [1/m^3]
Φ = 0.9
q = 1.602E-19 [coulomb]
V_{fb} = -0.4 [V]
W = 3.627E-07 [m]

No unit problems were detected.

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problem 15-27t

$Ipf = 2 \times 10^{21}$ [$1/m^2$-s]

$q = 1.602 \times 10^{-19}$ [Coulomb]

$I = q \cdot Ipf$

SOLUTION

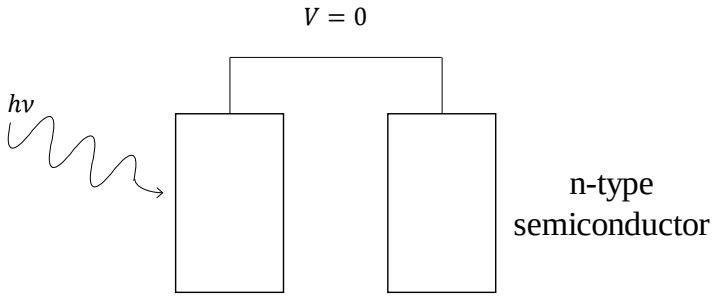
Unit Settings: SI C kPa kJ mass deg

I = 320.4 [A/m^2] Ipf = 2.000E+21 [$1/m^2$-s]

q = 1.602E-19 [Coulomb]

No unit problems were detected.

The open-circuit potential for the semiconductor electrode was determined in section 15.7. Another important characteristic is the short-circuit current. Develop and expression for this current.



To isolate the effect to the semiconductor electrode, assume $\eta_C = 0$ (no polarization of cathode) and no ohmic drop in solution, $\phi_{s,a} = \phi_{s,c}$

Definition of short circuit is $V_{cell} = 0$

$$V_{cell} = \phi_{metal} - \phi_{semi}$$

ϕ_{semi} is arbitrarily set to zero ⇒

$$\phi_{metal} = 0$$

$$\eta_{anode} = \left(\phi_{semi} - \phi_{s,a}\right) - U$$

$$\eta_{cathode} = (\phi_m - \phi_{s,c}) - U$$

$$\eta_c = 0 \Rightarrow \qquad \phi_{s,c} = -U$$

$$\phi_{s,a} = -U$$

$$\eta_a = (0 + U - U) = 0$$

$$i_{short} = i_{ph} + i_{CB}^0 \left(1 - exp\frac{-F\eta}{RT}\right) \quad (\eta \to 0)$$

$$i_{short} = i_{ph}$$

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```
"!PROBLEM 15-22"

eta_a=-phi_a-U

U=0.526 [V]
R=8.314 [J/mol-K]
T=298.15 [K]
F=96485 [coulomb/mol]

iph=250 [A/m^2]
icb=0.01 [A/m^2]

i=iph+icb*(1-exp(-F*eta_a/(R*T)))


"ohmic drop is solution"
kappa=6 [1/(ohm-m)]
L=2e-3 [m]
i=(kappa/L)*(phi_a-phi_c)

"load"
"Res=1 [ohm]"
i=phi_m/(Res*A)
A=1e-3 [m^2]

"cathode"
io=50 [A/m^2]
eta_c=phi_m-phi_c-U
i=-io*(exp(0.5*F*eta_c/(R*T))-exp(-0.5*F*eta_c/(R*T)))


"power"

P=i*phi_m

"polarizations"
"solution iR"
V_ohm=phi_a-phi_c

"open-circuit"

eta_oc=-(R*T/F)*ln(iph/icb+1)

"cell potential, another way"

Vcell=-eta_a-V_ohm+eta_c
va=-eta_a
vc=-eta_c
```

Parametric Table: iV curve

	i	ϕ_m	P	Res	V_{ohm}	η_c	vc	va	Vcell
	[A/m^2]	[V]	[W/m^2]	[Ω]	[V]	[V]	[V]	[V]	[V]
Run 1	243.9	0.0002439	0.05947	0.001	0.08129	-0.08345	0.08345	0.165	0.0002439
Run 2	243.9	0.0002739	0.0668	0.001123	0.08128	-0.08345	0.08345	0.165	0.0002739
Run 3	243.8	0.0003077	0.07503	0.001262	0.08128	-0.08345	0.08345	0.165	0.0003077
Run 4	243.8	0.0003456	0.08428	0.001417	0.08128	-0.08345	0.08345	0.1651	0.0003456
Run 5	243.8	0.0003882	0.09466	0.001592	0.08128	-0.08345	0.08345	0.1651	0.0003882

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Parametric Table: iV curve

	i [A/m^2]	ϕ_m [V]	P [W/m^2]	Res [Ω]	V_{ohm} [V]	η_c [V]	vc [V]	va [V]	Vcell [V]
Run 6	243.8	0.0004361	0.1063	0.001789	0.08127	-0.08345	0.08345	0.1652	0.0004361
Run 7	243.8	0.0004899	0.1194	0.002009	0.08127	-0.08344	0.08344	0.1652	0.0004899
Run 8	243.8	0.0005502	0.1341	0.002257	0.08126	-0.08344	0.08344	0.1653	0.0005502
Run 9	243.8	0.0006181	0.1507	0.002535	0.08126	-0.08344	0.08344	0.1653	0.0006181
Run 10	243.8	0.0006942	0.1692	0.002848	0.08125	-0.08344	0.08344	0.1654	0.0006942
Run 11	243.7	0.0007798	0.1901	0.003199	0.08125	-0.08343	0.08343	0.1655	0.0007798
Run 12	243.7	0.0008759	0.2135	0.003594	0.08124	-0.08343	0.08343	0.1655	0.0008759
Run 13	243.7	0.0009838	0.2398	0.004037	0.08123	-0.08342	0.08342	0.1656	0.0009838
Run 14	243.7	0.001105	0.2693	0.004535	0.08122	-0.08342	0.08342	0.1657	0.001105
Run 15	243.6	0.001241	0.3024	0.005094	0.08121	-0.08341	0.08341	0.1659	0.001241
Run 16	243.6	0.001394	0.3396	0.005722	0.0812	-0.08341	0.08341	0.166	0.001394
Run 17	243.6	0.001566	0.3814	0.006428	0.08119	-0.0834	0.0834	0.1662	0.001566
Run 18	243.5	0.001758	0.4282	0.007221	0.08118	-0.08339	0.08339	0.1663	0.001758
Run 19	243.5	0.001975	0.4809	0.008111	0.08116	-0.08338	0.08338	0.1665	0.001975
Run 20	243.4	0.002218	0.5399	0.009112	0.08114	-0.08337	0.08337	0.1667	0.002218
Run 21	243.4	0.002491	0.6062	0.01024	0.08112	-0.08336	0.08336	0.167	0.002491
Run 22	243.3	0.002797	0.6806	0.0115	0.0811	-0.08334	0.08334	0.1672	0.002797
Run 23	243.2	0.003141	0.764	0.01292	0.08107	-0.08333	0.08333	0.1675	0.003141
Run 24	243.1	0.003527	0.8576	0.01451	0.08104	-0.08331	0.08331	0.1679	0.003527
Run 25	243	0.003961	0.9625	0.0163	0.08101	-0.08329	0.08329	0.1683	0.003961
Run 26	242.9	0.004447	1.08	0.01831	0.08097	-0.08327	0.08327	0.1687	0.004447
Run 27	242.8	0.004993	1.212	0.02057	0.08092	-0.08324	0.08324	0.1692	0.004993
Run 28	242.6	0.005605	1.36	0.0231	0.08087	-0.08321	0.08321	0.1697	0.005605
Run 29	242.4	0.006292	1.525	0.02595	0.08082	-0.08318	0.08318	0.1703	0.006292
Run 30	242.3	0.007062	1.711	0.02915	0.08075	-0.08314	0.08314	0.171	0.007062
Run 31	242	0.007925	1.918	0.03275	0.08067	-0.0831	0.0831	0.1717	0.007925
Run 32	241.8	0.008893	2.15	0.03678	0.08059	-0.08304	0.08304	0.1725	0.008893
Run 33	241.5	0.009977	2.409	0.04132	0.08049	-0.08298	0.08298	0.1734	0.009977
Run 34	241.1	0.01119	2.698	0.04642	0.08037	-0.08292	0.08292	0.1745	0.01119
Run 35	240.7	0.01255	3.021	0.05214	0.08023	-0.08284	0.08284	0.1756	0.01255
Run 36	240.2	0.01407	3.38	0.05857	0.08008	-0.08274	0.08274	0.1769	0.01407
Run 37	239.7	0.01577	3.78	0.06579	0.07989	-0.08263	0.08263	0.1783	0.01577
Run 38	239	0.01767	4.223	0.07391	0.07968	-0.08251	0.08251	0.1799	0.01767
Run 39	238.3	0.01978	4.714	0.08302	0.07943	-0.08236	0.08236	0.1816	0.01978
Run 40	237.4	0.02214	5.256	0.09326	0.07913	-0.08218	0.08218	0.1834	0.02214
Run 41	236.3	0.02476	5.851	0.1048	0.07878	-0.08197	0.08197	0.1855	0.02476
Run 42	235.1	0.02767	6.504	0.1177	0.07836	-0.08172	0.08172	0.1877	0.02767
Run 43	233.6	0.03088	7.214	0.1322	0.07787	-0.08142	0.08142	0.1902	0.03088
Run 44	231.9	0.03443	7.983	0.1485	0.07729	-0.08106	0.08106	0.1928	0.03443
Run 45	229.8	0.03833	8.808	0.1668	0.07659	-0.08064	0.08064	0.1956	0.03833
Run 46	227.3	0.0426	9.684	0.1874	0.07578	-0.08013	0.08013	0.1985	0.0426
Run 47	224.4	0.04724	10.6	0.2105	0.07481	-0.07953	0.07953	0.2016	0.04724
Run 48	221.1	0.05227	11.55	0.2364	0.07369	-0.07882	0.07882	0.2048	0.05227
Run 49	217.1	0.05767	12.52	0.2656	0.07238	-0.07799	0.07799	0.208	0.05767
Run 50	212.6	0.06344	13.49	0.2984	0.07088	-0.07701	0.07701	0.2113	0.06344
Run 51	207.5	0.06956	14.44	0.3352	0.06918	-0.07588	0.07588	0.2146	0.06956
Run 52	201.8	0.07599	15.34	0.3765	0.06728	-0.0746	0.0746	0.2179	0.07599
Run 53	195.5	0.0827	16.17	0.4229	0.06518	-0.07314	0.07314	0.221	0.0827
Run 54	188.7	0.08964	16.92	0.4751	0.0629	-0.07152	0.07152	0.2241	0.08964
Run 55	181.4	0.09678	17.55	0.5337	0.06045	-0.06973	0.06973	0.227	0.09678
Run 56	173.6	0.1041	18.07	0.5995	0.05787	-0.06777	0.06777	0.2297	0.1041

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Parametric Table: iV curve

	i [A/m^2]	ϕ_m [V]	P [W/m^2]	Res [Ω]	V_{ohm} [V]	η_c [V]	vc [V]	va [V]	Vcell [V]
Run 57	165.5	0.1115	18.45	0.6734	0.05517	-0.06566	0.06566	0.2323	0.1115
Run 58	157.2	0.1189	18.69	0.7565	0.0524	-0.06341	0.06341	0.2347	0.1189
Run 59	148.7	0.1264	18.79	0.8498	0.04957	-0.06102	0.06102	0.237	0.1264
Run 60	140.2	0.1338	18.75	0.9545	0.04672	-0.05852	0.05852	0.239	0.1338
Run 61	131.6	0.1412	18.58	1.072	0.04388	-0.05593	0.05593	0.241	0.1412
Run 62	123.2	0.1484	18.28	1.205	0.04107	-0.05325	0.05325	0.2427	0.1484
Run 63	114.9	0.1555	17.88	1.353	0.03831	-0.05052	0.05052	0.2443	0.1555
Run 64	106.9	0.1625	17.36	1.52	0.03563	-0.04775	0.04775	0.2458	0.1625
Run 65	99.1	0.1692	16.77	1.707	0.03303	-0.04496	0.04496	0.2472	0.1692
Run 66	91.62	0.1757	16.1	1.918	0.03054	-0.04218	0.04218	0.2484	0.1757
Run 67	84.47	0.182	15.37	2.154	0.02816	-0.03942	0.03942	0.2496	0.182
Run 68	77.68	0.188	14.6	2.42	0.02589	-0.03671	0.03671	0.2506	0.188
Run 69	71.26	0.1937	13.81	2.719	0.02375	-0.03406	0.03406	0.2515	0.1937
Run 70	65.22	0.1992	12.99	3.054	0.02174	-0.0315	0.0315	0.2524	0.1992
Run 71	59.55	0.2043	12.17	3.43	0.01985	-0.02903	0.02903	0.2532	0.2043
Run 72	54.27	0.2091	11.35	3.854	0.01809	-0.02667	0.02667	0.2539	0.2091
Run 73	49.35	0.2136	10.54	4.329	0.01645	-0.02443	0.02443	0.2545	0.2136
Run 74	44.8	0.2178	9.76	4.863	0.01493	-0.02231	0.02231	0.2551	0.2178
Run 75	40.6	0.2218	9.003	5.462	0.01353	-0.02033	0.02033	0.2556	0.2218
Run 76	36.73	0.2254	8.278	6.136	0.01224	-0.01847	0.01847	0.2561	0.2254
Run 77	33.18	0.2287	7.588	6.893	0.01106	-0.01675	0.01675	0.2565	0.2287
Run 78	29.93	0.2318	6.937	7.743	0.009977	-0.01516	0.01516	0.2569	0.2318
Run 79	26.97	0.2346	6.325	8.697	0.008989	-0.01369	0.01369	0.2572	0.2346
Run 80	24.27	0.2371	5.754	9.77	0.008089	-0.01235	0.01235	0.2575	0.2371
Run 81	21.82	0.2394	5.223	10.97	0.007272	-0.01112	0.01112	0.2578	0.2394
Run 82	19.59	0.2415	4.732	12.33	0.006531	-0.01	0.01	0.2581	0.2415
Run 83	17.58	0.2434	4.28	13.85	0.00586	-0.008987	0.008987	0.2583	0.2434
Run 84	15.76	0.2452	3.864	15.56	0.005253	-0.008065	0.008065	0.2585	0.2452
Run 85	14.12	0.2467	3.484	17.48	0.004706	-0.007231	0.007231	0.2587	0.2467
Run 86	12.64	0.2481	3.137	19.63	0.004214	-0.006478	0.006478	0.2588	0.2481
Run 87	11.31	0.2494	2.821	22.05	0.00377	-0.005799	0.005799	0.259	0.2494
Run 88	10.11	0.2505	2.534	24.77	0.003372	-0.005188	0.005188	0.2591	0.2505
Run 89	9.041	0.2516	2.274	27.83	0.003014	-0.004639	0.004639	0.2592	0.2516
Run 90	8.078	0.2525	2.039	31.26	0.002693	-0.004146	0.004146	0.2593	0.2525
Run 91	7.214	0.2533	1.827	35.11	0.002405	-0.003704	0.003704	0.2594	0.2533
Run 92	6.441	0.254	1.636	39.44	0.002147	-0.003307	0.003307	0.2595	0.254
Run 93	5.749	0.2547	1.464	44.31	0.001916	-0.002952	0.002952	0.2596	0.2547
Run 94	5.129	0.2553	1.309	49.77	0.00171	-0.002634	0.002634	0.2596	0.2553
Run 95	4.576	0.2558	1.171	55.91	0.001525	-0.00235	0.00235	0.2597	0.2558
Run 96	4.081	0.2563	1.046	62.8	0.00136	-0.002096	0.002096	0.2597	0.2563
Run 97	3.639	0.2567	0.9341	70.55	0.001213	-0.001869	0.001869	0.2598	0.2567
Run 98	3.244	0.2571	0.834	79.25	0.001081	-0.001667	0.001667	0.2598	0.2571
Run 99	2.892	0.2574	0.7444	89.02	0.0009639	-0.001486	0.001486	0.2599	0.2574
Run 100	2.577	0.2577	0.6642	100	0.0008591	-0.001324	0.001324	0.2599	0.2577

Parametric Table: iV curve

	η_a [V]	η_{oc} [V]
Run 1	-0.165	-0.2602
Run 2	-0.165	-0.2602

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Parametric Table: iV curve

	η_a [V]	η_{oc} [V]
Run 3	-0.165	-0.2602
Run 4	-0.1651	-0.2602
Run 5	-0.1651	-0.2602
Run 6	-0.1652	-0.2602
Run 7	-0.1652	-0.2602
Run 8	-0.1653	-0.2602
Run 9	-0.1653	-0.2602
Run 10	-0.1654	-0.2602
Run 11	-0.1655	-0.2602
Run 12	-0.1655	-0.2602
Run 13	-0.1656	-0.2602
Run 14	-0.1657	-0.2602
Run 15	-0.1659	-0.2602
Run 16	-0.166	-0.2602
Run 17	-0.1662	-0.2602
Run 18	-0.1663	-0.2602
Run 19	-0.1665	-0.2602
Run 20	-0.1667	-0.2602
Run 21	-0.167	-0.2602
Run 22	-0.1672	-0.2602
Run 23	-0.1675	-0.2602
Run 24	-0.1679	-0.2602
Run 25	-0.1683	-0.2602
Run 26	-0.1687	-0.2602
Run 27	-0.1692	-0.2602
Run 28	-0.1697	-0.2602
Run 29	-0.1703	-0.2602
Run 30	-0.171	-0.2602
Run 31	-0.1717	-0.2602
Run 32	-0.1725	-0.2602
Run 33	-0.1734	-0.2602
Run 34	-0.1745	-0.2602
Run 35	-0.1756	-0.2602
Run 36	-0.1769	-0.2602
Run 37	-0.1783	-0.2602
Run 38	-0.1799	-0.2602
Run 39	-0.1816	-0.2602
Run 40	-0.1834	-0.2602
Run 41	-0.1855	-0.2602
Run 42	-0.1877	-0.2602
Run 43	-0.1902	-0.2602
Run 44	-0.1928	-0.2602
Run 45	-0.1956	-0.2602
Run 46	-0.1985	-0.2602
Run 47	-0.2016	-0.2602
Run 48	-0.2048	-0.2602
Run 49	-0.208	-0.2602
Run 50	-0.2113	-0.2602
Run 51	-0.2146	-0.2602
Run 52	-0.2179	-0.2602
Run 53	-0.221	-0.2602

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Parametric Table: iV curve

	η_a [V]	η_{oc} [V]
Run 54	-0.2241	-0.2602
Run 55	-0.227	-0.2602
Run 56	-0.2297	-0.2602
Run 57	-0.2323	-0.2602
Run 58	-0.2347	-0.2602
Run 59	-0.237	-0.2602
Run 60	-0.239	-0.2602
Run 61	-0.241	-0.2602
Run 62	-0.2427	-0.2602
Run 63	-0.2443	-0.2602
Run 64	-0.2458	-0.2602
Run 65	-0.2472	-0.2602
Run 66	-0.2484	-0.2602
Run 67	-0.2496	-0.2602
Run 68	-0.2506	-0.2602
Run 69	-0.2515	-0.2602
Run 70	-0.2524	-0.2602
Run 71	-0.2532	-0.2602
Run 72	-0.2539	-0.2602
Run 73	-0.2545	-0.2602
Run 74	-0.2551	-0.2602
Run 75	-0.2556	-0.2602
Run 76	-0.2561	-0.2602
Run 77	-0.2565	-0.2602
Run 78	-0.2569	-0.2602
Run 79	-0.2572	-0.2602
Run 80	-0.2575	-0.2602
Run 81	-0.2578	-0.2602
Run 82	-0.2581	-0.2602
Run 83	-0.2583	-0.2602
Run 84	-0.2585	-0.2602
Run 85	-0.2587	-0.2602
Run 86	-0.2588	-0.2602
Run 87	-0.259	-0.2602
Run 88	-0.2591	-0.2602
Run 89	-0.2592	-0.2602
Run 90	-0.2593	-0.2602
Run 91	-0.2594	-0.2602
Run 92	-0.2595	-0.2602
Run 93	-0.2596	-0.2602
Run 94	-0.2596	-0.2602
Run 95	-0.2597	-0.2602
Run 96	-0.2597	-0.2602
Run 97	-0.2598	-0.2602
Run 98	-0.2598	-0.2602
Run 99	-0.2599	-0.2602
Run 100	-0.2599	-0.2602

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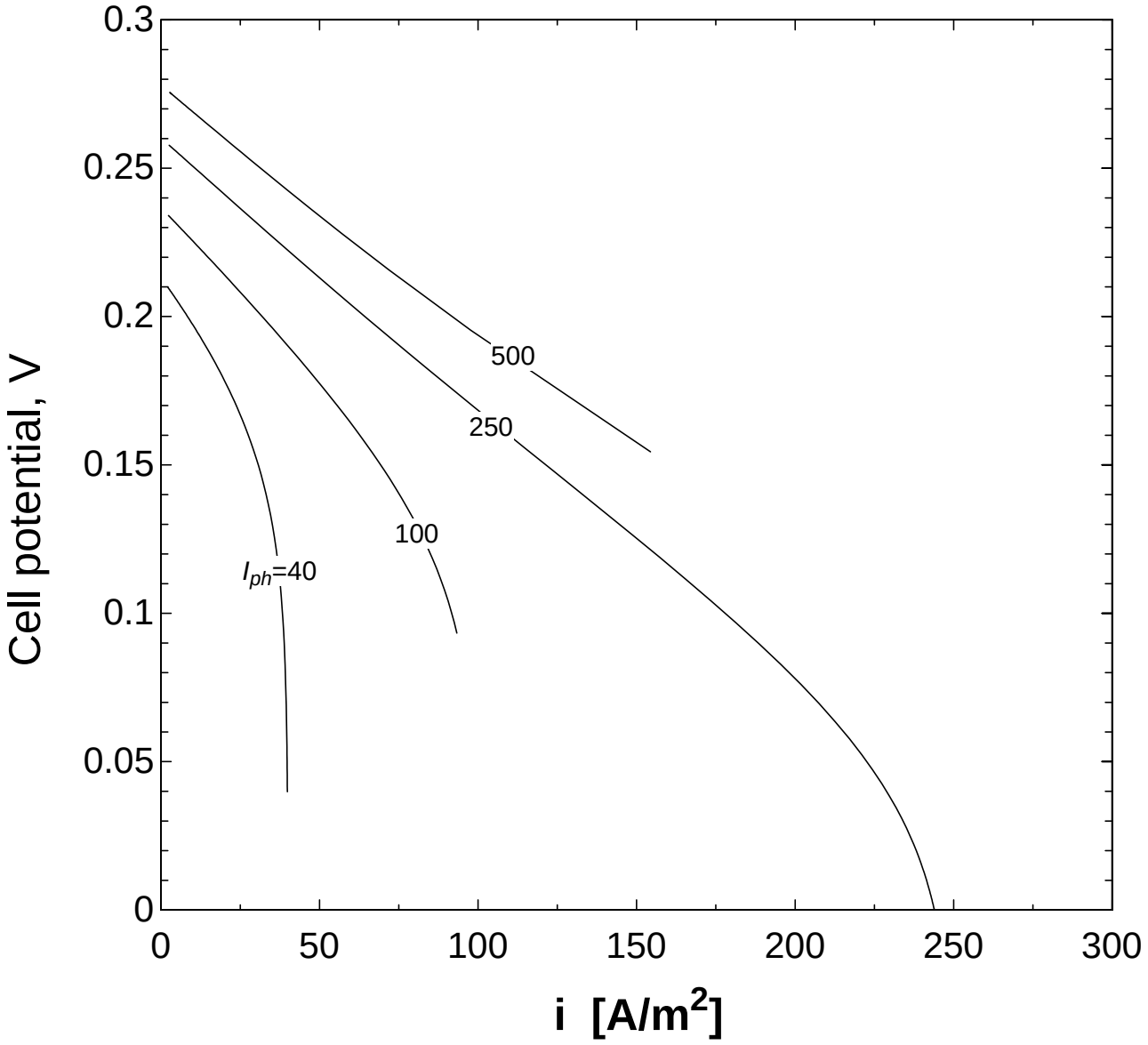

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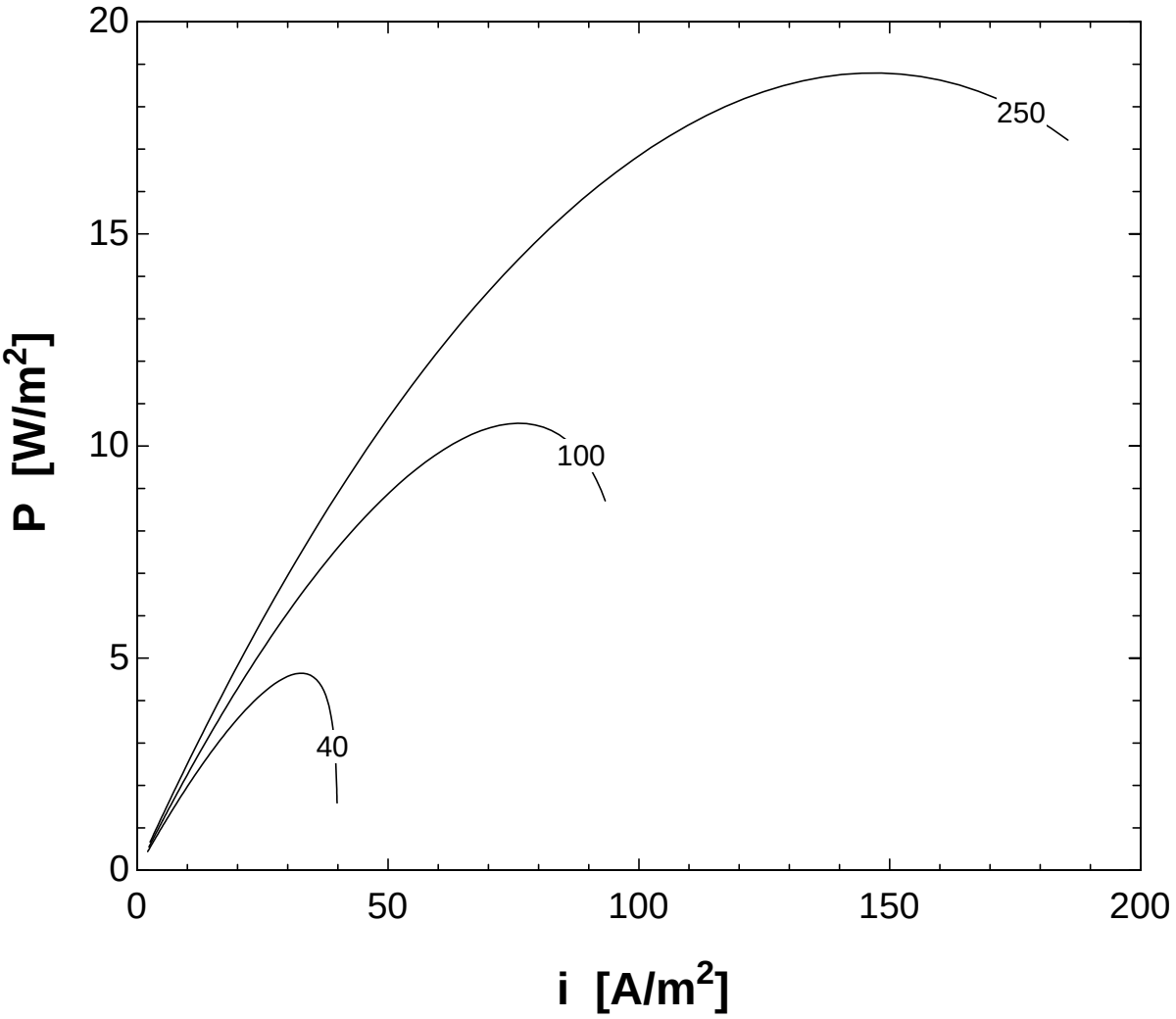

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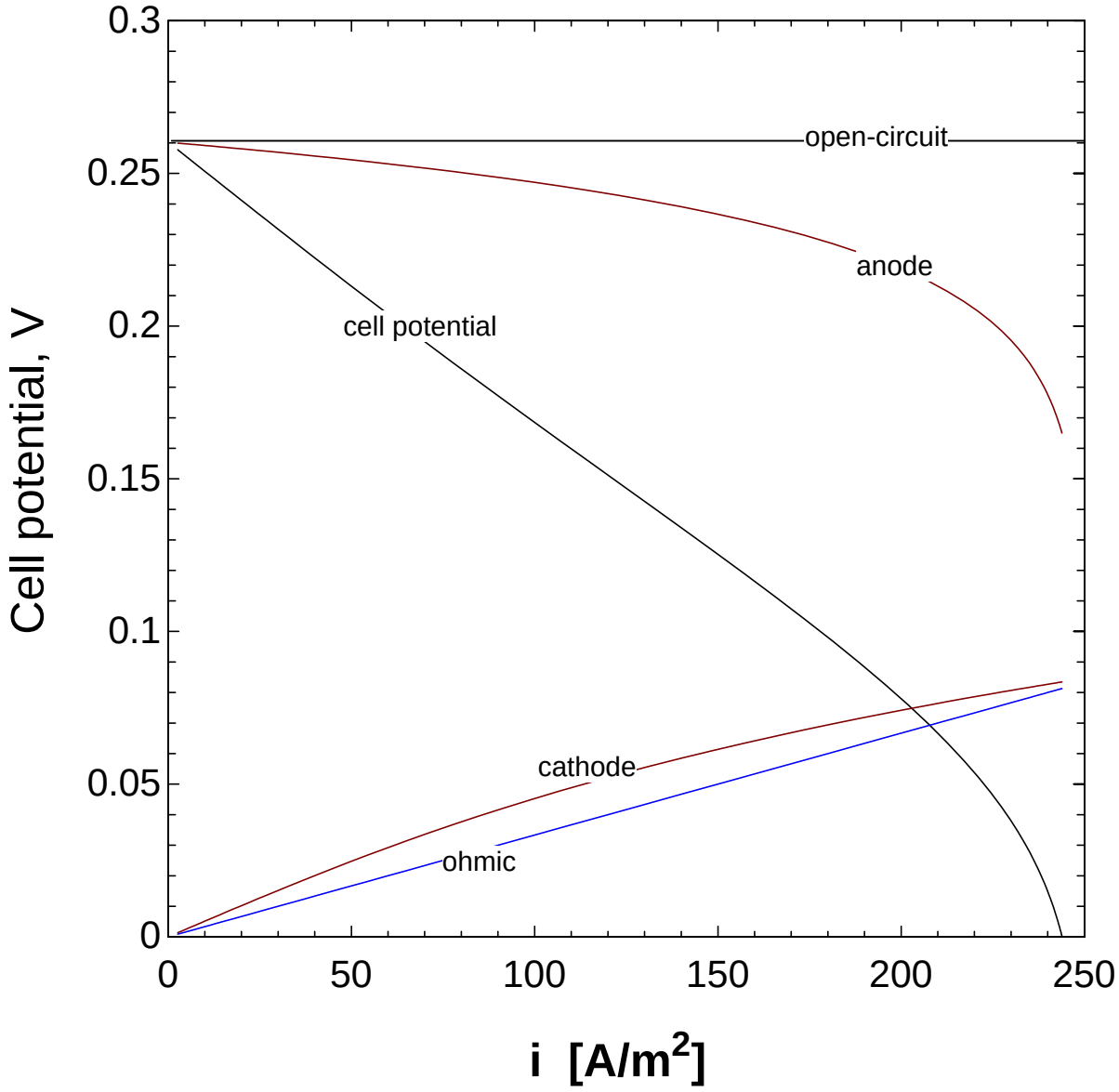


One method to determine V_{fb} is to measure the capacitance as was outlined in Illustration 15-3. Another approach is to measure the onset of photocurrent. The key to this method is to use monochromatic light of energy just slightly above the energy of the band gap. Under these conditions α is tiny and only a small amount of the incident light is absorbed in the depletion region. Starting with equation 15-22, show that the photocurrent is proportional to the width of the depletion region, *W*. Substitute this result into equation 15-6 to obtain the following relationship

$$\left(\frac{i_{ph}}{\alpha I_o''}\right)^2 = \frac{2\varepsilon}{qN_D}\left(\eta - V_{fb}\right)$$

$$\left|i_{ph}\right| = -qI_o^{"}\left\{1 - \frac{exp^{-\alpha W}}{1+\alpha L_p}\right\}$$

$$(eq.\ 15-22)$$

For small $\alpha,\ 1+\alpha L \approx 1$

$$exp^{-\alpha w} \approx 1 - \alpha W$$

$$i_{ph} \approx qI_o^{"}\alpha W$$

$$W = \left(\frac{2\varepsilon(\eta - V_{fb})}{qN_D}\right)^{1/2} \quad \text{(Eq. 15-6)}$$

Combining,

$$W = \frac{i_{ph}}{\alpha q I_o^{"}} = \left(\frac{2\varepsilon(\eta - V_{fb})}{qN_D}\right)^{1/2}$$

$$\frac{i_{ph}^2}{\alpha^2 I_o^{"2}} = \frac{2\varepsilon}{qN_D}\left(\eta - V_{fb}\right)$$

Problem 15-24

Given iph and overpotential data, and asked to determine the flat-band potential

η	i_{ph}	$(i_{ph})^2$
0.704	0.909	0.826281
0.557	0.845	0.714025
0.441	0.778	0.605284
0.321	0.706	0.498436
0.2	0.612	0.374544
0.129	0.553	0.305809

Equation $"(i_{ph})^2 = \text{constant} * \eta + \text{intercept}$

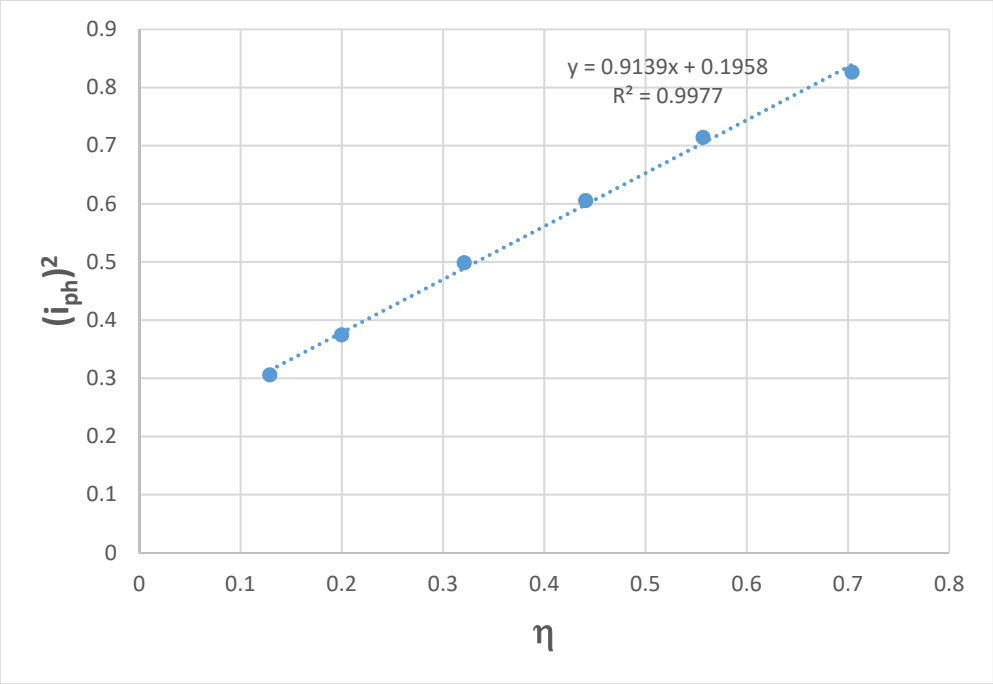
Intercept = -constant * V_{fb}

Use "Intercept" and "Slope" functions

Intercept 0.195822

Slope 0.91388

V_{fb} -0.21428 [V]



For an *n*-type semiconductor with a flat band potential of -0.4V, what is the relative concentration of electrons at the surface of a semiconductor compared to the bulk: 1) when there is no applied potential ($\eta = 0$) , and 2) at an applied overpotential of 0.2 V. Comment on the implications of these results on the kinetics of the reaction and the current behavior.

$$V_{fb} = -0.4$$

$$\frac{n_s}{n_b} = exp\left(\frac{-Q}{kT}(\eta - V_{fb})\right)$$
$$= \exp\left(\frac{-F}{RT}(\eta - V_{fb})\right)$$

1)

For $\eta = 0$,

$$\frac{n_s}{n_b} = exp\left(\frac{-F}{RT}(0.4)\right)$$
$$\frac{n_s}{n_b} = 1.71 \times 10^{-7}$$

2)

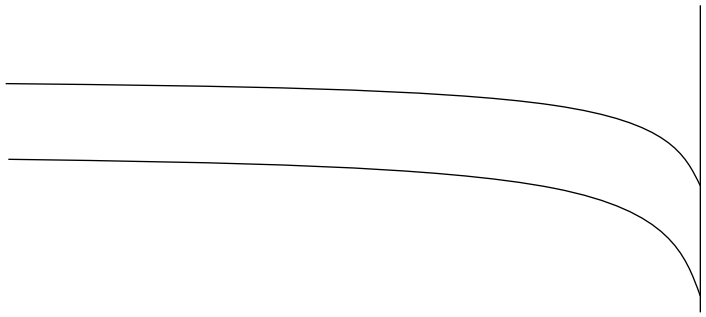
For $\eta = 0.2$,

$$\frac{n_s}{n_b} = exp\left(\frac{-F}{RT}(0.2 - (-0.4))\right)$$
$$= 7.12 \times 10^{-11}$$

Shows that our previous assumption of a zero electron concentration is reasonable, as are the implications as already discussed.

In section 15.3 the starting point for developing the description of the depletion layer was that the associated energy level of the redox couple was between the conduction and valence bands. What would change if the potential of the redox couple were either above the conduction band or below the valence band? Would it change with the doping (*n* or *p*)?

If the energy of the redox couple were above that of an n-type semiconductor, electrons would transfer from the solution to the semiconductor, which would now have an enrichment layer rather than a depletion layer. Band bending would be in the opposite direction.



By the way, the higher energy corresponds to a lower potential.

Similarly, for a p-type semiconductor, an energy below the fermi-level of the semiconductor would lead to transfer of holes from the solution to the semiconductor, also causing carrier enrichment and band bending in the opposite direction from that observed previously for a redox couple with energy in the band gap. Yes, type matters.

Please address the following qualitative questions:

a. What is corrosion and why does it occur?
b. What is the driving force for corrosion?
c. How would you expect temperature to affect the rate of corrosion for a structure in the ocean? Describe in detail the aspects of corrosion that would be affected by temperature and how temperature might affect those aspects.

a. Corrosion is the spontaneous oxidation of a metal in its environment. This anodic reaction is accompanied by a cathodic reaction. It occurs because the metal is not thermodynamically stable in many environments.

b. For the corrosion to occur spontaneously, the change in Gibbs energy for the overall reaction must be negative. We can express this change in terms of potential for electrochemical corrosion.

c. There are several physical processes involved in corrosion in seawater and all are influenced by temperature.

Factor	Effect
conductivity	ionic conductivity increases with increasing temperature. A higher conductivity would reduce ohmic losses and increase the rate of corrosion
oxygen solubility	gas solubility decreases with increasing temperature. Likely cathodic reaction is the reduction of oxygen. With lower solubility the limiting current would be lower
diffusivity of oxygen	increases with temperature, but effect of solubility is larger
exchange current density	the exchange current density would increase with temperature causing more rapid corrosion.

An aqueous solution at pH=5 contains 0.1M ferric ion. From a thermodynamic perspective, is there a driving force for corrosion if this solution flows through nickel tubing? Support your answer quantitatively. Would you expect corrosion to occur?

$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	Wikipedia
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25	Wikipedia

There is a large driving thermodynamic driving force for corrosion at standard conditions. Because the voltage difference is so large, correction of the standard potentials for concentration is not necessary.

At pH = 5, the stable nickel species above the equilibrium potential is the soluble ion Ni^{2+} (see Figure 16-2). Therefore, it is not likely that a passive layer will form and corrosion is expected to occur.

Magnesium is being used as a structural material in cars, for example, because it is light and has good structural properties. However, there is concern regarding corrosion. Is that concern warranted? Please support your response quantitatively.

From Appendix A, the standard reduction potential is

$Mg^{2+} + 2e^- \rightarrow Mg$	-2.357

Following Illustration 16-1, there would be a large thermodynamic driving force (large positive potential) to react with oxygen from air. Perhaps more importantly, the potential of Mg is well below the stability window of water and Mg reacts with water to dissolve (corrode) the Mg and evolve hydrogen gas. So yes, the concerned is warranted. Mg and its alloys do form passivation layers; however, these layers are only robust enough to protect the metal in relatively mild environments. Additionally, there would be concern with galvanic corrosion if Mg were in contact with another metal, such as steel.

Using Gibbs energy values, determine the standard potential for the reaction represented by line 10 of Figure 16-2. Derive an expression for the equilibrium potential of the reaction represented by Line 10 in Figure 16-2 as a function of pH. What assumption was made to get the values shown in the figure? What impact would a change in this assumption have on the equilibrium potential?

$$Ni + 2H_2O = HNiO_2^- + 3H^+ + 2e^-$$

$$2H^+ + 2e^- = H_2$$

$$Ni + 2H_2O = H_2NiO_2(aq) + H_2$$

$$\Delta G_{RX} = \sum s_i \Delta G_{fi}$$

$$\Delta G_f^{H_2NiO_2} = -599.3\ kJ$$

$$\Delta G_f^{H_2O} = -237.129\ kJ$$

$$\Delta G_{RX} = (-599.3) - 2(237.129)$$

$$= -125\ kJ$$

$$U^\theta = -\frac{\Delta G}{nF} = \frac{125{,}000}{(2)96485} = 0.648V$$

$$U = U^\theta + \frac{RT}{2F}\ln[H^+]^3[HNiO_2^-]$$

Assume $[HN_iO_2^-] = 10^{-6}$

$$U = 0.648 + \frac{3}{2}\frac{RT}{F}2.303\log[H^+]$$

$$+\frac{1}{2}\frac{RT}{F}\ln(10^{-6})$$

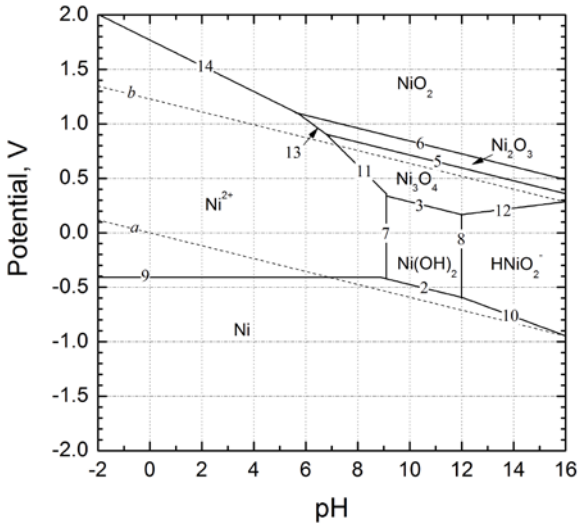
$$U = 0.648 + 0.1774 - 0.0887\ pH$$

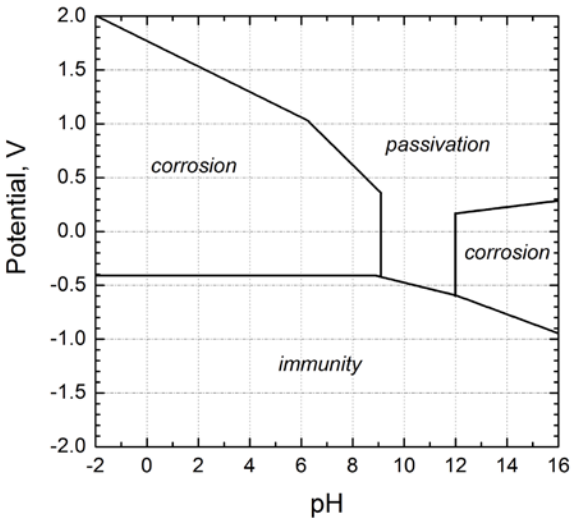
$$U = 0.471 - 0.0887\ pH$$

Assumed $[HN_iO_2^-] = 10^{-6}$. Larger values will shift the line to more positive values.

Using the Pourbaix diagram for nickel (Figure 16-2), is the corrosion of nickel in aqueous solutions more likely to be problematic in highly acidic or highly basic solutions? Please justify your response. You should consider the stability of water.

Corrosion will be more of a problem in highly acidic solutions. At low pH, corrosion begins at about -0.4 V. Importantly, this value is below the hydrogen line, which means that Ni will corrode by reducing water to form hydrogen gas. In contrast, water is stable at high pH where the soluble $HNiO_2^-$ species is formed. Therefore, a cathodic reaction other than water reduction is necessary for corrosion to occur.





1. There is a large driving force for the corrosion of zinc in deaerated aqueous solution, where the primary cathodic reaction would be hydrogen evolution. However, zinc is stable in such environments. The following kinetic parameters apply: for the zinc reaction, α_a = 1.5 and i_o = 0.10 A·cm^{-2}; for hydrogen evolution, α_c = 0.5 and i_o = 10^{-9} A·cm^{-2}. Assume Tafel kinetics, calculate the following:
   a. The corrosion potential
   b. The corrosion current for zinc
   c. The corrosion rate of zinc in mm/yr

   Why is the corrosion rate of zinc so low?

		H2	io	1.00E-09	A/cm2
Need equilibrium potentials			alpha	0.5	
For Zn, assume concentration of 10^-6 in solution		Zn	io	0.1	A/cm2
Uzn	-0.940468785		alpha	1.5	

For H2, assume pH 7

Uh2 -0.4144

Calculate corrosion potential by setting anodic and cathodic currents equal. Used Solver to find Vcorr

V	-0.940465178		
Zn	0.100021073	2.80958E-05	A/cm2
H2	-3.55925E-14	-2.80958E-05	A/cm2
Sum		-3.90746E-16	Solver

Can't use Tafel because the potential is too close to the equation potential for Zn

Use BV Instead

Zn corrosion limited by H_2 rate, which is low.

a) Corrosion potential

Can't use Tafel equation for Zn since it is too close to the equilibrium potential. Use BV instead.

Zinc is essentially at its equilibrium potential and the corrosion rate is the H_2 evolution rate at that potential.

b) Zinc corrosion current: 2.81e-5 A/cm2

c) Corrosion rate:

rho	7.13	g/cm3
M	65.39	g/mol
n	2	eq/mol

Corrosion Rate

-0.421094823 mm/yr

The corrosion rate is low because of the slow kinetics of H2 evolution on Zn.

Note: The i_o used in this problem for hydrogen evolution on Zn is actually high.

Therefore, the corrosion rate is even lower than that reported here.

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Problem 16-7

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

$F = 96485$ [coulomb/mol]

a, use equation 16-6 to calculate corrosion current

$aa = 0.5$

$ac = 0.5$

$ba = 0.12$ [V]

$bc = 0.12$ [V]

$Ua = -0.44$ [V] *iron*

$Uc = 0$ [V] *hydrogen reaction*

$ioa = 0.002$ [A/m^2]

$ioc = 0.1$ [A/m^2]

$$g1 = \frac{ba}{ba + bc}$$

$$g2 = \frac{bc}{ba + bc}$$

$$i_{corr} = ioa^{g1} \cdot ioc^{g2} \cdot \mathbf{exp}\left[2.303 \cdot \left[\frac{Uc - Ua}{ba + bc}\right]\right]$$

part a continued, calculate the corrosion potential, equation 16-5

$$V_{corr} = \frac{ac \cdot Uc + aa \cdot Ua}{aa + ac} + R \cdot \frac{T}{F \cdot (aa + ac)} \cdot \mathbf{ln}\left[\frac{ioc}{ioa}\right]$$

part b, use Faraday's law to convert current to corrosion rate in mm/year

$\rho = 7874$ [kg/m^3]

$M = 0.0556$ [kg/mol]

$n = 2$

$$\dot{l} = \frac{M}{\rho} \cdot \frac{i_{corr}}{n \cdot F}$$

$cf1 = 1000$ [mm/m]

$cf2 = 3600 \cdot 24 \cdot 365 \cdot 1$ [s/year]

$cr = \dot{l} \cdot cf1 \cdot cf2$

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part c, make plot using table, vary potential from 0 to -0.6 V

$$ic = ioc \cdot \mathbf{exp}\left[-ac \cdot F \cdot \left[\frac{V - Uc}{R \cdot T}\right]\right]$$

$$ia = ioa \cdot \mathbf{exp}\left[aa \cdot F \cdot \left[\frac{V - Ua}{R \cdot T}\right]\right]$$

$$it = |ia - ic|$$

V=-0.25 [V]

SOLUTION

Unit Settings: SI C kPa kJ mass deg

(Table 1, Run 100)

aa = 0.5
ac = 0.5
ba = 0.12 [V]
bc = 0.12 [V]
cf1 = 1000 [mm/m]
cf2 = 3.154E+07 [s/year]
cr = 1.113 [mm/year]
F = 96485 [coulomb/mol]
g1 = 0.5
g2 = 0.5
ia = 3.008E+09 [A/m^2]
ic = 3.496E-10 [A/m^2]
ioa = 0.002 [A/m^2]
ioc = 0.1 [A/m^2]
it = 3.008E+09 [A/m^2]
i_{corr} = 0.9642 [A/m^2]
$\dot{I}$ = 3.528E-11 [m/s]
M = 0.0556 [kg/mol]
n = 2
R = 8.314 [J/mol-K]
ρ = 7874 [kg/m^3]
T = 298 [K]
Ua = -0.44 [V]
Uc = 0 [V]
V = 1 [V]
V_{corr} = -0.1195 [V]

No unit problems were detected. (1 disabled)

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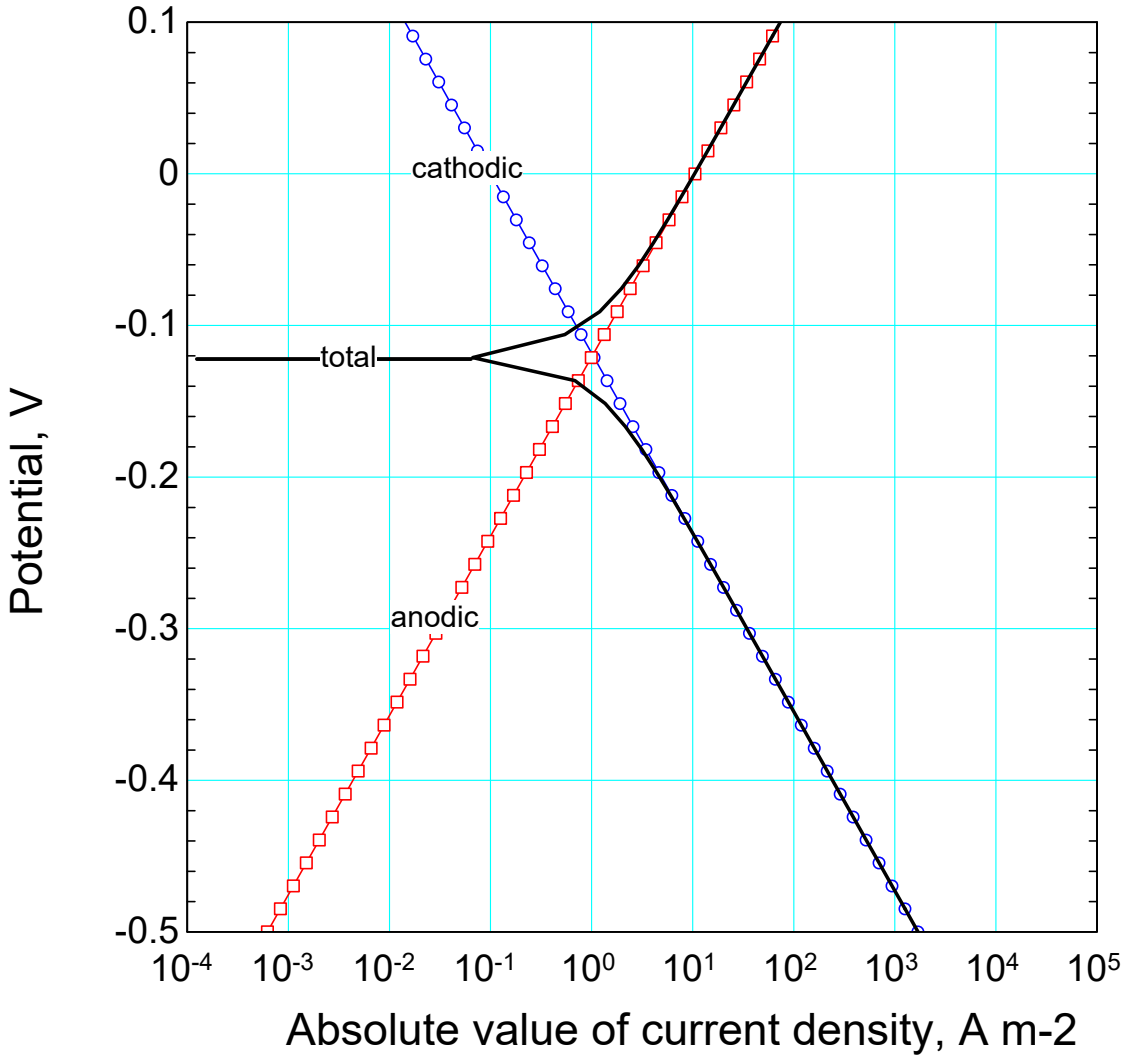

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Problem 16-8, seawater corrosion

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

$F = 96485$ [coulomb/mol]

anodic dissolution of iron

cathodic hydrogen evolution and oxygen reduction

$Ua = -0.5$ [V] *iron dissolution*

$aa = 0.5$

$ioa = 0.014$ [A/m^2]

$Uc1 = 0$ [V] *hydrogen reaction*

$ac1 = 0.5$ *hydrogen evolution*

$ioc1 = 0.000001$ [A/m^2]

$Uc2 = 0.401$ [V] *oxygen reduction reaction*

$ac2 = 1$ *oxgyen reduction*

$ioc2 = 1.0 \times 10^{-16}$ [A/m^2]

make plot using table, vary potential from 0 to -0.6 V

$$ic1 = ioc1 \cdot \mathbf{exp}\left[-ac1 \cdot F \cdot \left[\frac{V - Uc1}{R \cdot T}\right]\right]$$

$$ic2 = \left[1 - \frac{ic2}{i_{lim}}\right] \cdot ioc2 \cdot \mathbf{exp}\left[-ac2 \cdot F \cdot \left[\frac{V - Uc2}{R \cdot T}\right]\right]$$

$i_{lim} = 0.3$ [A/m^2]

$ic = ic1 + ic2$

$$ia = ioa \cdot \mathbf{exp}\left[aa \cdot F \cdot \left[\frac{V - Ua}{R \cdot T}\right]\right]$$

$it = |ia - ic|$

V=-0.005 [V]

SOLUTION

Unit Settings: SI C kPa kJ mass deg

(Table 1, Run 100)

aa = 0.5 ac1 = 0.5

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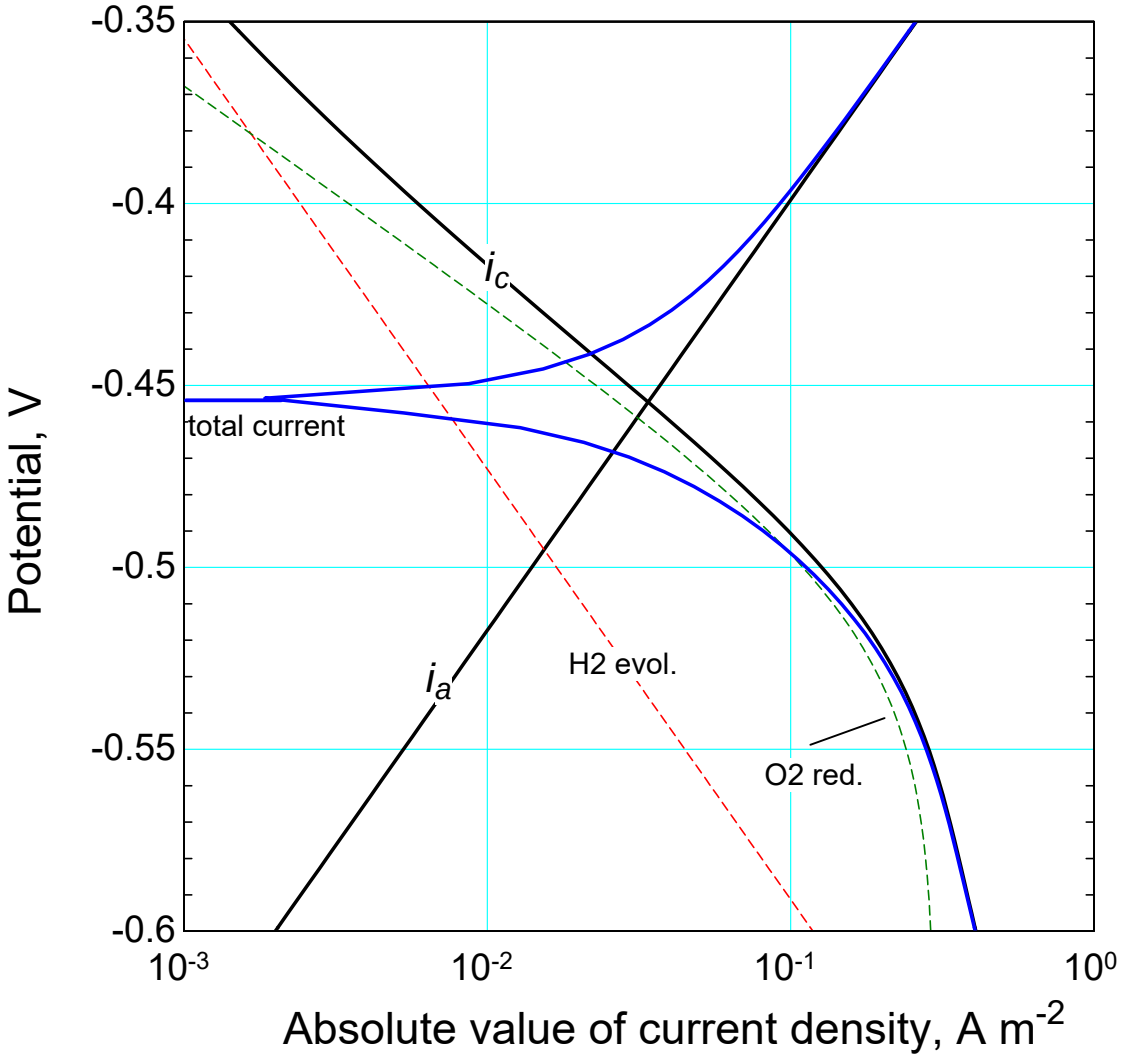
ac2 = 1
ia = 0.6877 [A/m^2]
ic1 = 0.0003443 [A/m^2]
ioa = 0.014 [A/m^2]
ioc2 = 1.000E-16 [A/m^2]
i_{lim} = 0.3 [A/m^2]
T = 298 [K]
Uc1 = 0 [V]
V = -0.3 [V]

F = 96485 [coulomb/mol]
ic = 0.000416 [A/m^2]
ic2 = 0.00007175 [A/m^2]
ioc1 = 0.000001 [A/m^2]
it = 0.6873 [A/m^2]
R = 8.314 [J/mol-K]
Ua = -0.5 [V]
Uc2 = 0.401 [V]

No unit problems were detected.



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Problem 16-9

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

$F = 96485$ [coulomb/mol]

use equation 16-6 to calculate corrosion current

$aa = 1$

$ac = 0.25$

$$ba = \ln[10] \cdot R \cdot \frac{T}{aa \cdot F}$$

$$bc = \ln[10] \cdot R \cdot \frac{T}{ac \cdot F}$$

$Ua = -0.126$ [V] *lead*

$Uc = 0$ [V] *hydrogen reaction*

$ioa = 1$ [A/m^2]

$ioc = 0.000001$ [A/m^2]

$$g1 = \frac{ba}{ba + bc}$$

$$g2 = \frac{bc}{ba + bc}$$

$$i_{corr} = ioa^{g1} \cdot ioc^{g2} \cdot \exp\left[2.303 \cdot \left(\frac{Uc - Ua}{ba + bc}\right)\right]$$

next, calculate the corrosion potential, equation 16-5

$$V_{corr} = \frac{ac \cdot Uc + aa \cdot Ua}{aa + ac} + R \cdot \frac{T}{F \cdot [aa + ac]} \cdot \ln\left[\frac{ioc}{ioa}\right]$$

use Faraday's law to convert current to corrosion rate in mm/year

$\rho = 11340$ [kg/m^3]

$M = 0.2072$ [kg/mol]

$n = 2$

$$\dot{l} = \frac{M}{\rho} \cdot \frac{ia}{n \cdot F}$$

$cf1 = 1000$ [mm/m]

$cf2 = 3600 \cdot 24 \cdot 365 \cdot 1$ [s/year]

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$$cr = \dot{i} \cdot cf1 \cdot cf2$$

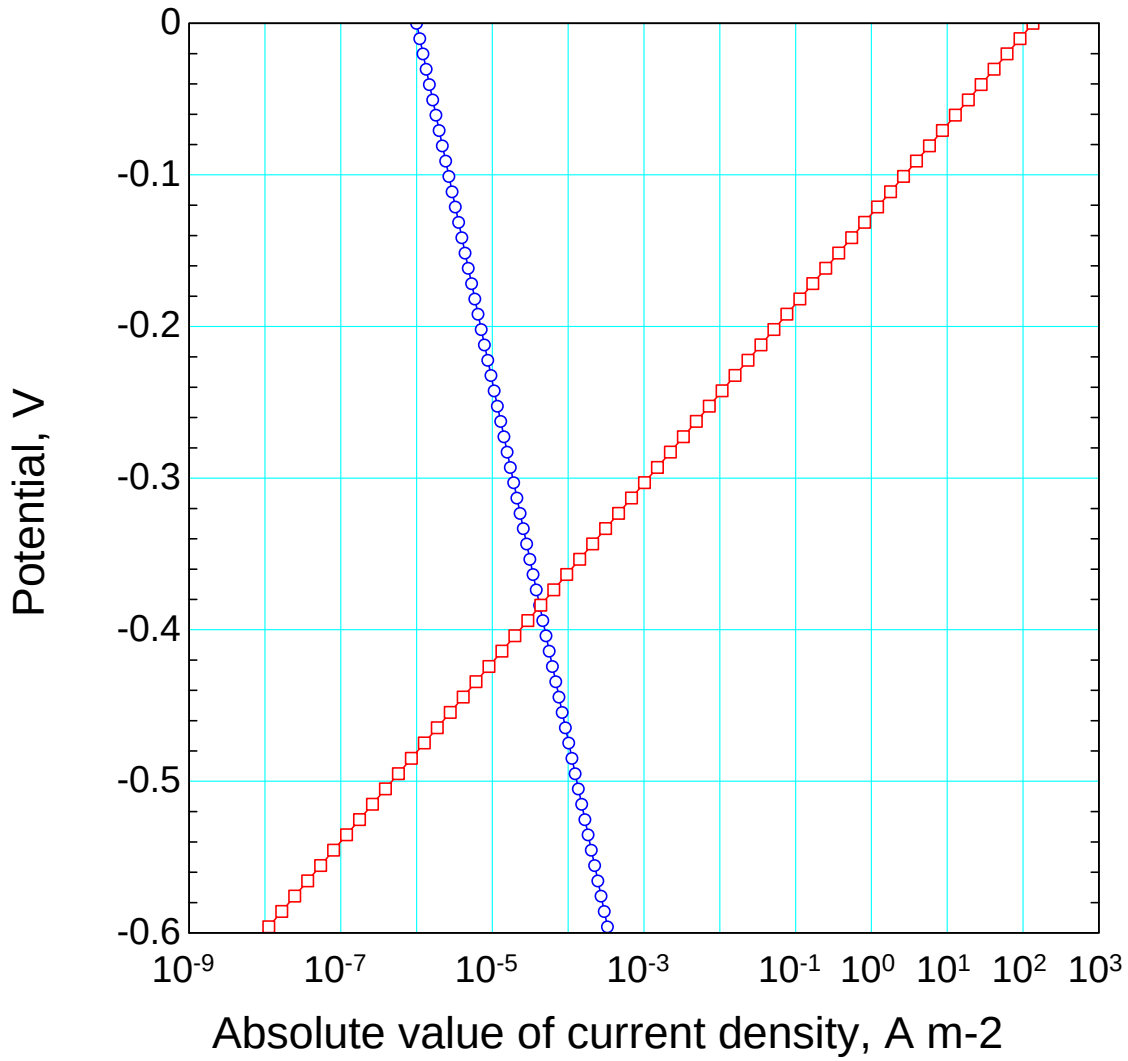
$$crc = \frac{M}{\rho} \cdot \frac{ic}{n \cdot F} \cdot cf1 \cdot cf2$$

make plot using table, vary potential from 0 to -0.6 V

$$ic = ioc \cdot \mathbf{exp}\left[-ac \cdot F \cdot \left(\frac{V - Uc}{R \cdot T}\right)\right]$$

$$ia = ioa \cdot \mathbf{exp}\left[aa \cdot F \cdot \left(\frac{V - Ua}{R \cdot T}\right)\right]$$

$V = -0.3$ [V]



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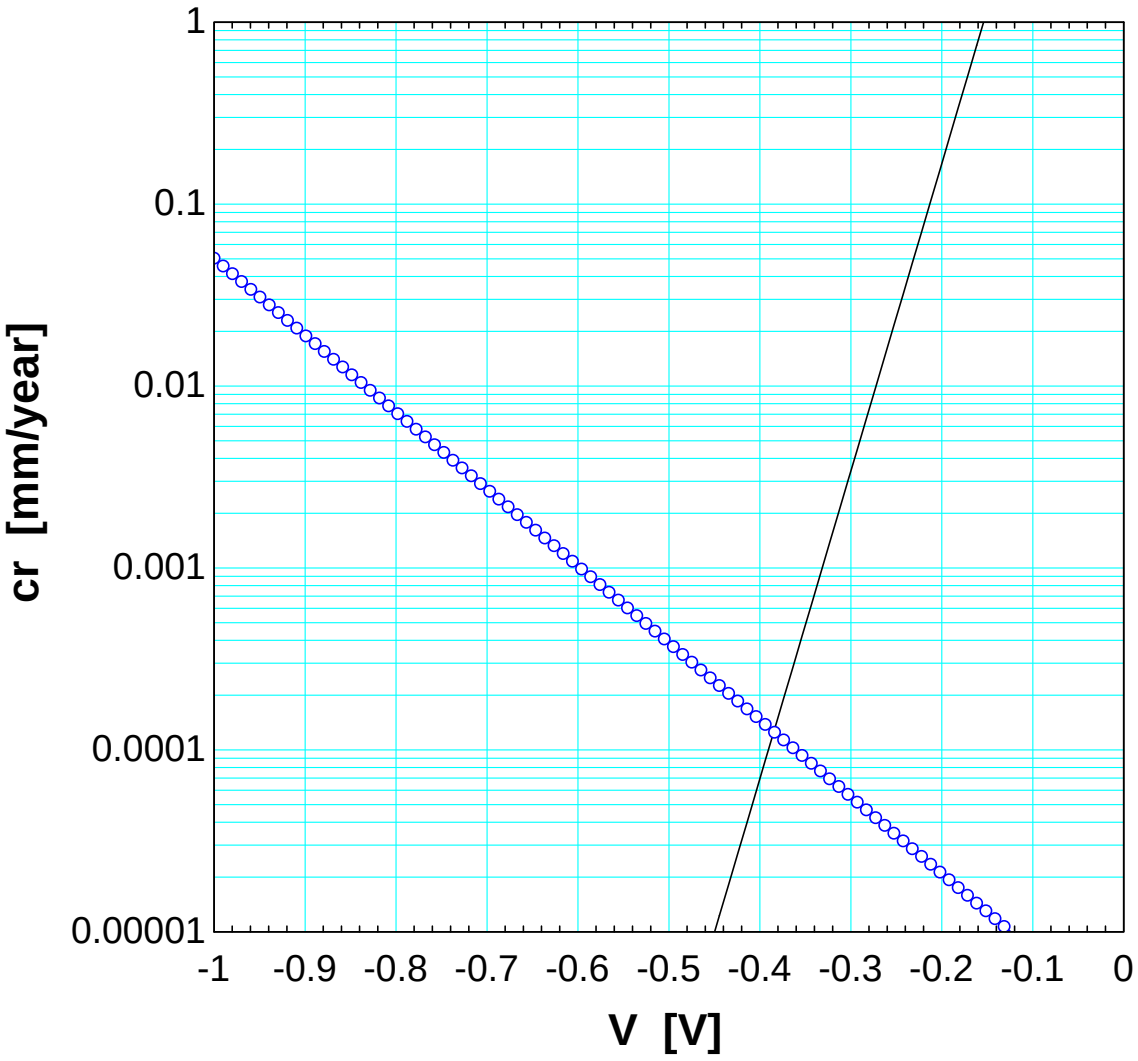

In solutions where a passivation layer is not formed on zinc, the corrosion potential is found to be very close to the equilibrium potential for zinc. What can you infer about the kinetics for the anodic (dissolution of zinc) compared to the kinetics for the cathodic (hydrogen evolution or oxygen reduction) reactions?

If the corrosion potential is close to the equilibrium potential for zinc, this indicates that the kinetics for the cathodic reaction are slow by comparison. This occurs because the exchange-current density for hydrogen on zinc is very small (see chapter 3). It is also possible that there is little oxygen available for reduction.

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Problem 16-11

$F = 96485$ [coulomb/mol]

$R = 8.314$ [J/mol-K]

$T = 298$ [K]

calculate mass transfer rate of oxygen to copper surface

$D = 0.03$ [m]

$V_{inf} = 2$ [m/s]

$co = 0.3$ [mol/m^3]

$T1 = 290$ [K]

$p1 = 100$ [kPa]

$\rho = \rho(\text{water}, T = T1, P = p1)$

$\mu = \textbf{Visc}(\text{water}, T = T1, P = p1)$

$Do = 1.0 \times 10^{-9}$ [m^2/s]

$$Re = V_{inf} \cdot D \cdot \frac{\rho}{\mu}$$

$Pr = \textbf{Pr}(\text{water}, T = T1, P = p1)$

$$Sc = \frac{\mu}{\rho \cdot Do}$$

$$NuD = 0.3 + 0.62 \cdot Re^{0.5} \cdot \frac{Pr^{0.3333}}{\left[1 + \left[\frac{0.4}{Pr}\right]^{0.6667}\right]^{0.25}} \cdot \left[1 + \left[\frac{Re}{282000}\right]^{0.625}\right]^{0.8}$$ *correlation from literature for flow over cylinder*

$$Sh = NuD \cdot \left[\frac{Sc}{Pr}\right]^{0.333}$$ *use Chilton Colburn Analogy*

$$Sh = kc \cdot \frac{D}{Do}$$

$i_{lim} = n \cdot F \cdot kc \cdot co$

$n = 4$

Assuming Tafel kinetics, develop expressions for anodic and cathodic currents

$Ua = 0.337$ [V] *copper dissolution*

$aa = 0.5$

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$ioa = 0.00005$ [A/m^2]

Uc1=-0.472 [V]; hydrogen reaction (note that the hydrogen reaction is not needed for this problem)
ac1=1; hydrogen evolution
ioc1=8e-7 [A/m^2]; Bockris, 0.01 N KOH

*ic1=ioc1*exp(-ac1*F*(V-Uc1)/R/T)*

$Uc2 = 0.76$ [V] *oxygen reduction reaction*

$ac2 = 1$ *oxgyen reduction*

$ioc2 = 1.0 \times 10^{-7}$ [A/m^2]

$$ic2 = \left[1 - \frac{ic2}{i_{lim}}\right] \cdot ioc2 \cdot \mathbf{exp}\left[-ac2 \cdot F \cdot \left[\frac{V - Uc2}{R \cdot T}\right]\right]$$

$ic = ic2$ *hydrogen reaction is neglected*

$$ia = ioa \cdot \mathbf{exp}\left[aa \cdot F \cdot \left[\frac{V - Ua}{R \cdot T}\right]\right]$$

V=0.5 [V]

$\rho_{cu} = 8960$ [kg/m^3]

$M = 0.06354$ [kg/mol]

$na = 2$

$$\dot{i} = \frac{M}{\rho_{cu}} \cdot \frac{ia}{na \cdot F}$$

$cf1 = 1000$ [mm/m]

$cf2 = 3600 \cdot 24 \cdot 365 \cdot 1$ [s/year]

$cr = \dot{i} \cdot cf1 \cdot cf2$

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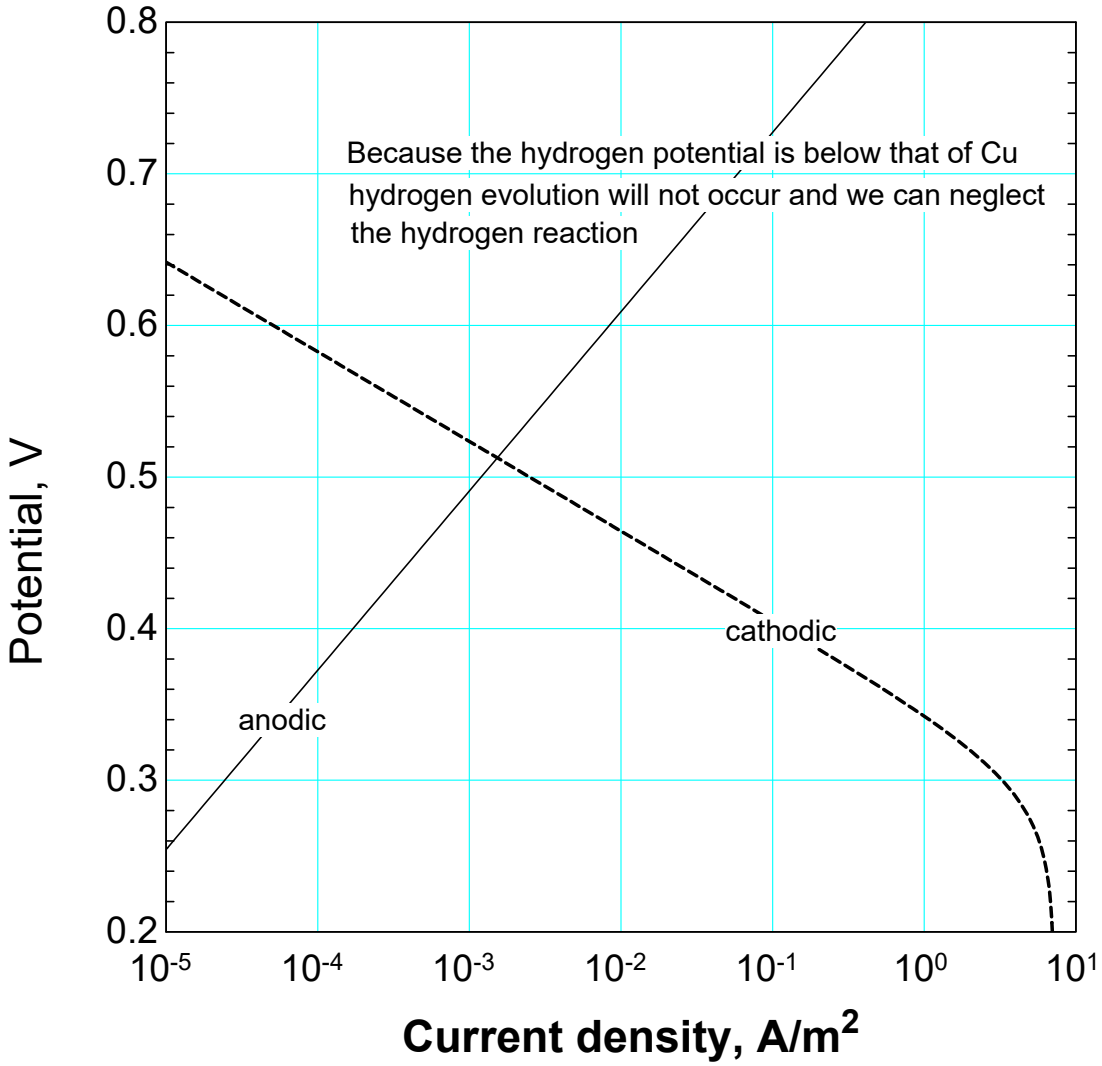


The following composite corrosion polarization curve is measured for Fe in deaerated acid solution by changing the current and measuring the corresponding potential. From the semi-log plot, please determine the following:

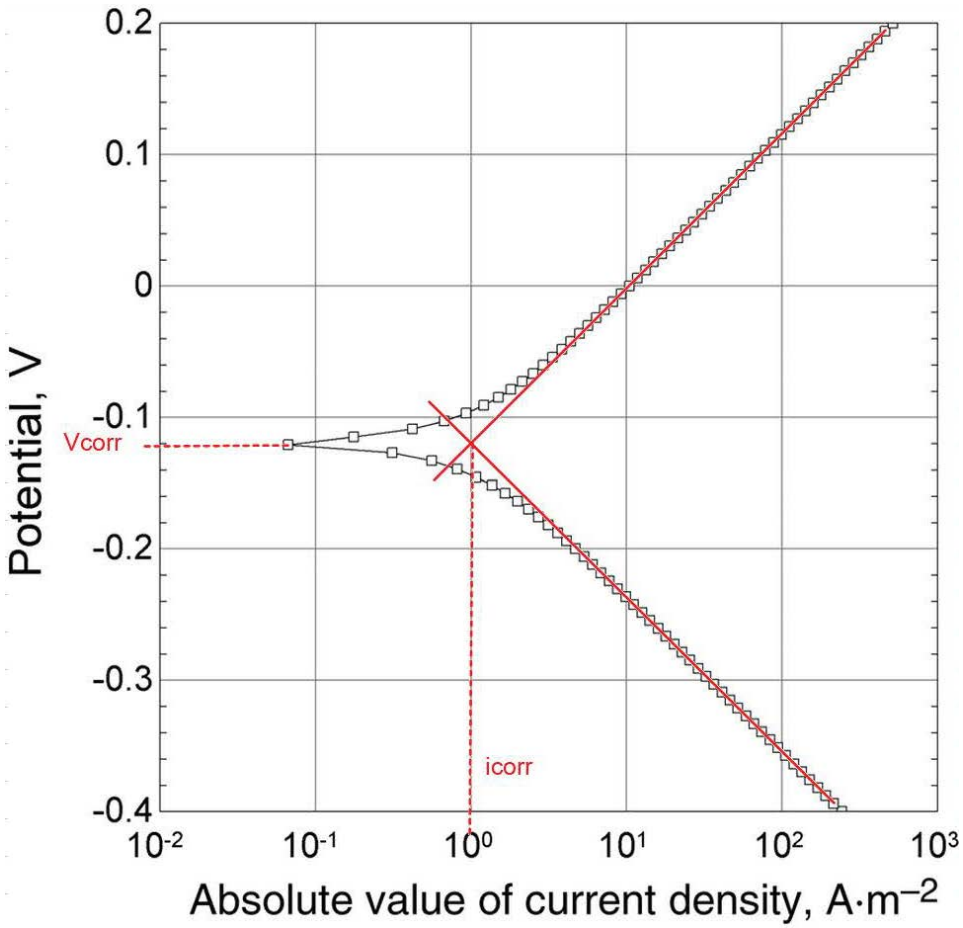
a. The corrosion potential relative to SHE

b. The corrosion current

c. The Tafel slope of the anodic reaction

d. The Tafel slope of the cathodic reaction

Make sure to state any assumptions that you make.



a) Corrosion potential – see graph
From the figure $V_{corr} \approx -0.12$

b) Also from the figure, $i_{corr} = 10° = 1\frac{A}{m^2}$

c) $V = f(\log i)$

$Slope = \dfrac{\Delta V}{\log i}$

For the anodic curve, $\frac{0-(-0.12)}{\log(10)-\log(1)} = 0.120$

$= 120 \dfrac{mV}{decade}$

d) $\frac{-0.24-(-0.12)}{\log(10)-\log(1)} = -0.120$

(negative sign often not reported)

Tafel slope for the cathodic reaction is also 120mV/decade

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Problem 16-13

F = 96485 [coulomb/mol]

R = 8.314 [J/mol-K]

T = 298 [K]

Reaction 1

a1 = 0.5

ac1 = 0.5

U1t = 0.233 [V]

io1 = 200 [A/m^2]

$$i1 = io1 \cdot c1^{1.5} \cdot c4^{0.5} \cdot \left[\exp\left[a1 \cdot F \cdot \left[\frac{V - U1}{R \cdot T}\right]\right] - \exp\left[-ac1 \cdot F \cdot \left[\frac{V - U1}{R \cdot T}\right]\right]\right]$$

Reaction 2

a2 = 0.5

ac2 = 0.5

U2t = 0.441 [V]

io2 = 1 [A/m^2]

$$i2 = io2 \cdot c1^{1.5} \cdot c2^{0.5} \cdot c4^{0.5} \cdot \left[\exp\left[a2 \cdot F \cdot \left[\frac{V - U2}{R \cdot T}\right]\right] - \exp\left[-ac2 \cdot F \cdot \left[\frac{V - U2}{R \cdot T}\right]\right]\right]$$

Reaction 3

a3 = 0.5

ac3 = 0.5

U3t = 0.419 [V]

io3 = 0.5 [A/m^2]

$$i3 = io3 \cdot c1 \cdot c3^{0.5} \cdot c4^{0.5} \cdot \left[\exp\left[a3 \cdot F \cdot \left[\frac{V - U3}{R \cdot T}\right]\right] - \exp\left[-ac3 \cdot F \cdot \left[\frac{V - U3}{R \cdot T}\right]\right]\right]$$

Reaction 4

a4 = 0.5

ac4 = 0.5

U4t = 0.431 [V]

io4 = 0.5 [A/m^2]

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$$i4 = io4 \cdot c1^{0.5} \cdot c5^{0.5} \cdot c4^{0.5} \cdot \left[\exp\left[a4 \cdot F \cdot \left[\frac{V - U4}{R \cdot T}\right]\right] - \exp\left[-ac4 \cdot F \cdot \left[\frac{V - U4}{R \cdot T}\right]\right]\right]$$

Reaction 5

$a5 = 0.5$

$ac5 = 0.5$

$U5t = 0.435$ [V]

$io5 = 1$ [A/m^2]

$$i5 = io5 \cdot c4^{0.5} \cdot c6^{0.5} \cdot c4^{0.5} \cdot \left[\exp\left[a4 \cdot F \cdot \left[\frac{V - U4}{R \cdot T}\right]\right] - \exp\left[-ac4 \cdot F \cdot \left[\frac{V - U4}{R \cdot T}\right]\right]\right]$$

$i1p = |i1|$ *this is the anodic reaction*

$i2p = |i2|$

$i3p = |i3|$

$i4p = |i4|$

$i5p = |i5|$

$ic = |i2 + i3 + i4 + i5|$

concentrations provided

$c1 = 1.23$ *Cl-*

$c2 = 0.067$ *Cu2+*

$c3 = 0.1897$ *CuCl+*

$c4 = 0.02$ *CuCl32-*

$c5 = 0.1517$ *CuCl2*

$c6 = 0.071$

$c7 = 0.0009$ *typo in text*

adjust potentials

$$U1 = U1t - R \cdot \frac{T}{F} \cdot \ln\left[\frac{c1^3}{c4}\right]$$

$$U2 = U2t - R \cdot \frac{T}{F} \cdot \ln\left[\frac{c4}{c1^3 \cdot c2}\right]$$

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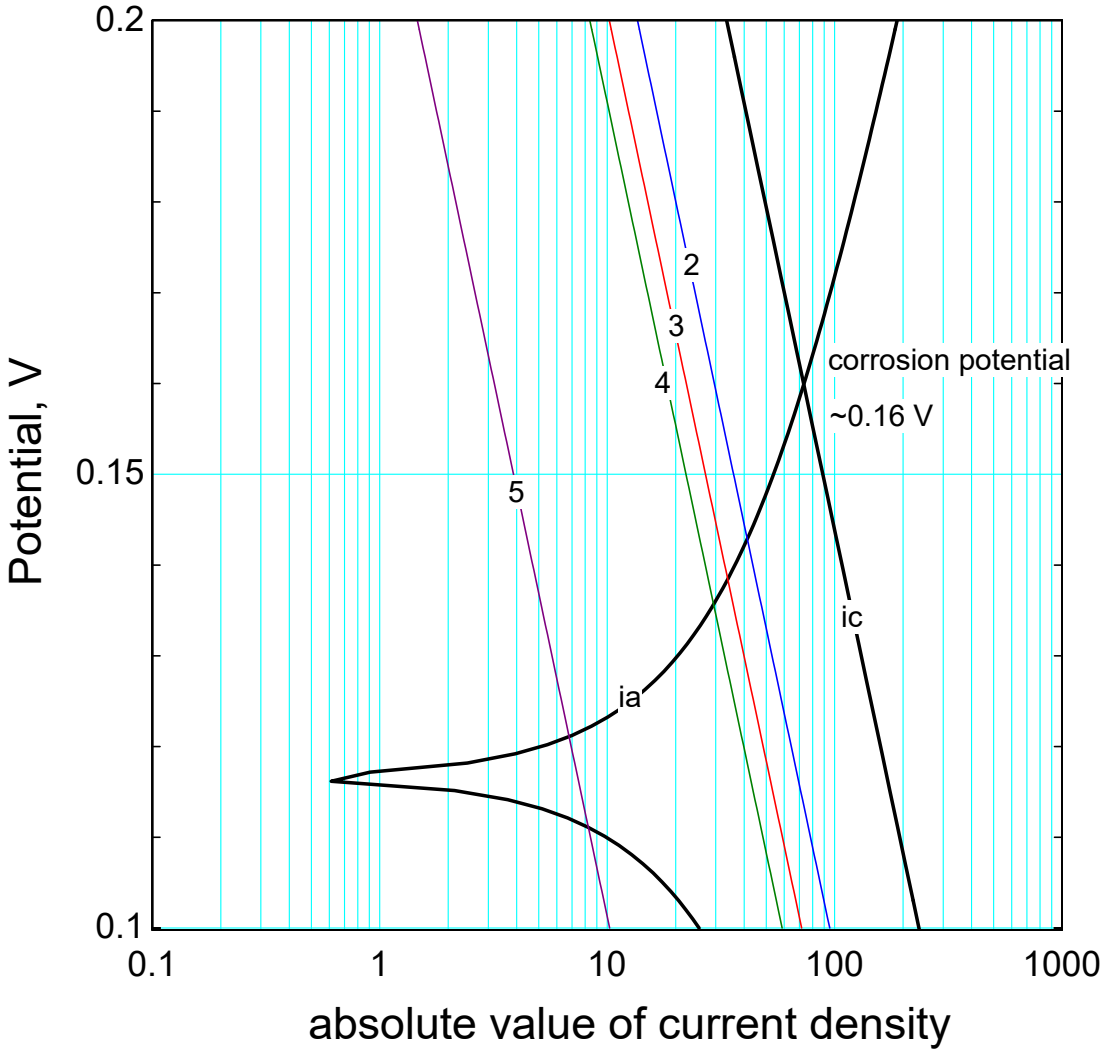
$$U3 = U3t - R \cdot \frac{T}{F} \cdot \ln\left[\frac{c4}{c1^{2} \cdot c3}\right]$$

$$U4 = U4t - R \cdot \frac{T}{F} \cdot \ln\left[\frac{c4}{c1 \cdot c5}\right]$$

$$U5 = U5t - R \cdot \frac{T}{F} \cdot \ln\left[\frac{c4}{c6}\right]$$



1. A simplified cell, which results in a uniform current density during corrosion of the full surfaces, can be used to examine galvanic corrosion. If the two metals are not connected, each metal corrodes independently of the other. However, if a highly conductive wire is used to connect the two metals, they become galvanically coupled and their corrosion rates change dramatically. Exam corrosion of iron and zinc using the parameters from Figure 16-10.

   The conductivity of the solution is constant and equal to 0.08 $S \cdot m^{-1}$. The electrodes are infinite plates separated by a distance of 3 cm.

   Please calculate the following:

   a. The uncoupled corrosion potential (SHE) and corrosion current density ($A \cdot m^{-2}$) for each of the two metals.

   b. The rate of corrosion for the coupled system.

You will need to account for the ohmic losses in solution, which will allow you to relate the potential of the solution at one electrode to that at the other. The sum of the cathodic and anodic currents on the two electrodes together must equal zero. Report the potential of each electrode *vs*. a Ag/AgCl reference electrode located at the electrode surface. Also report the specific anodic and cathodic currents for each electrode.

Here are the expressions used in Figure 16.10, where the data for Zn in the paper was refit

$$i_{Fe} = 10^{\frac{(V-0.07413)}{0.1005}} - 10^{\frac{-(V+10.42)}{2.09}} - 10^{\frac{-(V+1.463)}{0.1534}}$$

$$i_{Zn} = 10^{\frac{(V+0.607)}{0.0292}} - 10^{\frac{-(V+1.591)}{0.1253}}$$

These represent the total current on the electrode and include both the anodic and cathodic current
The first term in each equation represents the anodic current for each electrode material
The potentials in the above expressions are phi electrode - phi SHE just outside double layer
These expressions should have been given to students as part of the problem

Corrosion Potentials and Currents

Zn Electrode

Vcorr	-0.7930	Corrosion potential for zinc [V]
itotal	-7.86E-13	Use solver to determine the corrosion potential by setting itotal = 0
icorr	4.28E-07	Zn dissolution rate [A/cm2]

The corrosion current (dissolution rate) was obtained by substituting the corrosion potential into the expression for the anodic current

Fe Electrode

Vcorr	-0.4070	Corrosion potential for iiron [V]
itotal	-1.59826E-15	Use solver to determine the corrosion potential
icorr	1.63E-05	Fe dissolution rate [A/cm2]

Galvanic System

L	3	cm
K	0.0008	S/cm

The potential of both metals is assumed to be the same and equal to zero.

Vzn	-0.7410	Potential difference between zinc and SHE (varied so total cur = 0)
izn	2.56121E-05	Net current at zinc electrode (includes both anodic and cathodic)
Vfe	-0.6449	Potential difference between iron and SHE. Impacted by IR drop.
ife	-2.56121E-05	Net current at the iron electrde

izn + ife	-6.04914E-16	Total current = net at zinc and net at iron.

Solver is used to find phizn that gives a total current of zero.
Assuming that the metals are a zero, the solution potential at the zinc electrode is 0.7410 (positive)
and that at the iron electrode is 0.6449 (also positive)

Zn Dissolution	2.57766E-05	[A/cm2]
Fe Dissolution	7.00E-08	Value is probably too high since likely below the equilibrium potential
		Results from using a Tafel expression outside the allowable range
		Fe dissolution is zero

Potential of Zinc electrode vs. Ag/AgCl (sat. KCl)	-0.9380	[V]
Potential of Iron electrode vs. Ag/AgCl (sat. KCl)	-0.8419	[V]

Ag/AgCl Sat KC 0.197 vs. SHE

Describe the difference between immunity and passivity. Explain the relationship between these conditions and anodic and cathodic protection strategies for corrosion mitigation.

Immunity means that corrosion is not favored thermodynamically, and therefore the metal is protected. Passivity occurs in an environment where corrosion is thermodynamically favored, but where rate is so low that the metal is largely protected. This occurs when an insoluble oxide layer forms on the surface and greatly reduces the rate of corrosion.

Where does the cathodic reaction occur during pitting corrosion? Why does it occur there? What implications does this have for the growth of multiple corrosion pits on a surface?

The cathodic reaction takes place both inside and outside the pit. The surface area of the metal that is passive and not part of the pit is very large compared to that of the pit. Therefore, the majority of the cathodic reaction (e.g., oxygen reduction) takes place outside of the pit since a large surface area is required so that the total cathodic current, which has a low current density, matches the high dissolution of metal in the pit.

For a surface with multiple pits, the required size of the surface outside of the pits increases as the pits continue to grow until there is no long sufficient area outside of the pits to support all of the growing pits. This can lead to the death of some of the pits or can result in passivation of the top portion of some of the pits, resulting in deep growth of narrow pits (very bad).

Why does galvanic coupling increase the corrosion rate of the more active metal?

When the two metals are in direct contact, the “metal” potentials will be the same. Corrosion of both metals can occur, but the overpotential for the less noble (more active) metal will be higher and therefore the corrosion rate will be larger.

Why does the overpotential of the more active metal increase? Coupling of an active metal with a more noble metal provides additional area for the cathodic reaction to occur, which increases the overpotential of the active metal so that the anodic and cathodic currents remain equal. The kinetics of the cathodic reaction may also be faster on the more noble metal. As long as the dissolution rate of the more active metal is fast enough to match the cathodic reaction on both the active and noble metals, the more noble metal will not corrode while the corrosion rate of the active metal will increase due to galvanic coupling.

The corrosion rate of magnesium increases dramatically when it is coupled with iron, even if the area of the iron is just a fraction of that of the magnesium. Please explain why this might be so.

Mg is more active than iron, as seen by comparing the standard potentials

$Mg^{2+} + 2e^- \rightarrow Mg$	-2.357
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440

The reason that a small amount of iron makes such a difference in the Mg corrosion rate when the two metals are galvanically coupled is because the kinetics of hydrogen evolution are much faster on iron than on Mg, and the driving force for corrosion between hydrogen (water reduction) and Mg is large.

Explain why cathodic current is required in order to cathodically protect metal structures.

The idea behind cathodic protection is to lower the potential of the metal that is being protected to either reduce, V1, or eliminate, V2, corrosion. Examining the Evan plot, figure 16-15, it is evident that if the potential is reduced, then the cathode current will increase.

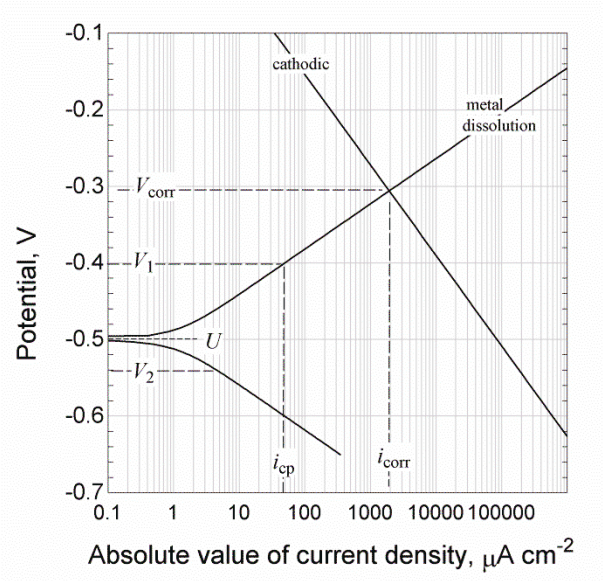


Figure 16-1 Evans diagram showing corrosion potential and the reduction of corrosion current with a reduction in potential.

Does a sacrificial anode represent anodic protection or cathodic protection? Please explain.

A sacrificial anode represents “cathodic protection.” By using a more active metal that preferentially corrodes, the potential of the metal is reduced. A lower (more cathodic) potential results in a lower corrosion current of the metal that is being protected. Also, the cathodic current increases, but this cathodic current is balanced by a small corrosion current of the metal being protected and a large corrosion current of the sacrificial material.

You have been assigned to develop a system to protect a stationary sea oil drilling platform located in 400 m deep water. Based on your understanding of sacrificial anodes,

a. what costs are associated with 1) installation of a sacrificial anode system, and 2) operation of a sacrificial anodic protection system?
b. Repeat part (a) for ICCP systems.
c. Based on your answers to (a) and (b), which strategy do you expect to be more expensive? Which would be easier to implement?

a. installation of sacrificial anode system should be simple. The sacrificial material is simply attached directly to the metal being protected. This could be done prior to installation of the structure on the sea floor. The major drawback for sacrificial systems is that the material needs to be replaced periodically.
b. ICCP would be more costly to install. Inert electrodes are needed as well as a power supply for potential control. Assuming that stable electrodes are used that do not require replacement, the ICCP should require lower maintenance.
c. ICCP is a better choice other than for short term applications because of the difficulty of replacing the sacrificial anodes at large ocean depths.

```python
# Problem 16-22
# Import Libraries
import numpy as np
# Parameters Given in Problem
ioa = 0.002 #A/m2
aa = 0.5  #alpha value for anodic reaction
ac = 0.5  #alpha value for hydrogen reaction
ioh2 = 0.05 #A/m2
UFe = -0.64  #V
pH = 8.0
io2 = -0.2 #A/m2
#
# Additional constants and parameters
F = 96485 #Faraday's constant
R = 8.314 #J/mol K  Gas constant
T = 298.15 #assumed Temp (K)
rho = 7874 #Fe density (kg/m3)
M = 0.0556 #kg/mol
n = 2
#
# Determine equilibrium voltage for H2 reaction at pH 8
UH2 = 0 - 0.059*pH
print ('Equilibrium potential of hydrogen reaction  ',UH2,'V')
# calculate current density for 0.1 mm/yr and corresponding Vcorr
cf1 = 365*24*3600 #s/yr
icorr = 0.1e-3*rho/M*n*F/cf1  #A/m2
print ('Corrosion current  ',icorr,'A/m2')
vcorr = R*T/F/aa*np.log(icorr/ioa) + UFe
#
# Since the equilibrium voltage of hydrogen is lower than vcorr, hydrgen
# does not contribute to the cathodic current
iH2 = 0.0
ic = iH2 + io2 #total cathodic current due to h2 and o2
#
# Calculate the anodic current that must be supplied by ICCP system
i_impressed = -(icorr + ic)
print ('The impressed current is ',i_impressed,'A/m2')
#
# Calculate vcorr vs. SCE
Vcorr = vcorr - 0.244  #V vs. SCE
print ('The corrosion potential is  ',Vcorr,'V vs. SCE')
#
# Part (a) Lines below from Console Window
# Equilibrium potential of hydrogen reaction   -0.472 V
# Corrosion current   0.0866570316805916 A/m2
# The corrosion potential is   -0.446349160011 V
# The impressed current is  0.1133429683194084 A/m2
#
# Part (b)
# The corrosion potential is   -0.690349160011 V vs. SCE
#
# Part (c)
# -850 mV vs. SCE would be overprotective for this system.  This would
# increase costs, but would protect the iron better than required.
# H2 would likely be important at the lower potential, and may cause problems.
```

ICCP is to be used to protect a steel dock structure in seawater. The surface area of the structure is 15 m 2 . The anodes available are platinized Ti with an OD of 2.5 cm and a length of 1 m. Specific kinetic data and conductivity data for your system are not available.

a. Please recommend an appropriate anode configuration.

b. If electricity is $0.05/kWhr, how much would it cost to operate this system for a year (assume continuous operation for the entire year and no losses in rectifying the electricity)? Assume a potential drop of 20 V.

c. What factors might influence your placement of the ICCP anodes?

$$Dock\ Surface\ Area = 15m^2$$

$$Anode\ Surface\ Area = \left(\frac{\pi(2.5)}{100} \cdot 1\right) m^2$$

$$= 0.0785m^2$$

a) $Current\ required\ for\ protection = 0.1 \frac{A}{m^2}$
(see illustration 16-6)

$$Total\ current\ for\ protection = \left(0.1 \frac{A}{m^2}\right)(15m^2)$$
$$= 1.5\ A$$

From Table 16-1, platinized electrodes have a range from 250-2000 A/m^2

Choose 1000 A/m^2

Anode area required $\frac{1.5\ A}{1000\ A/m^2} = 0.0015m^2$

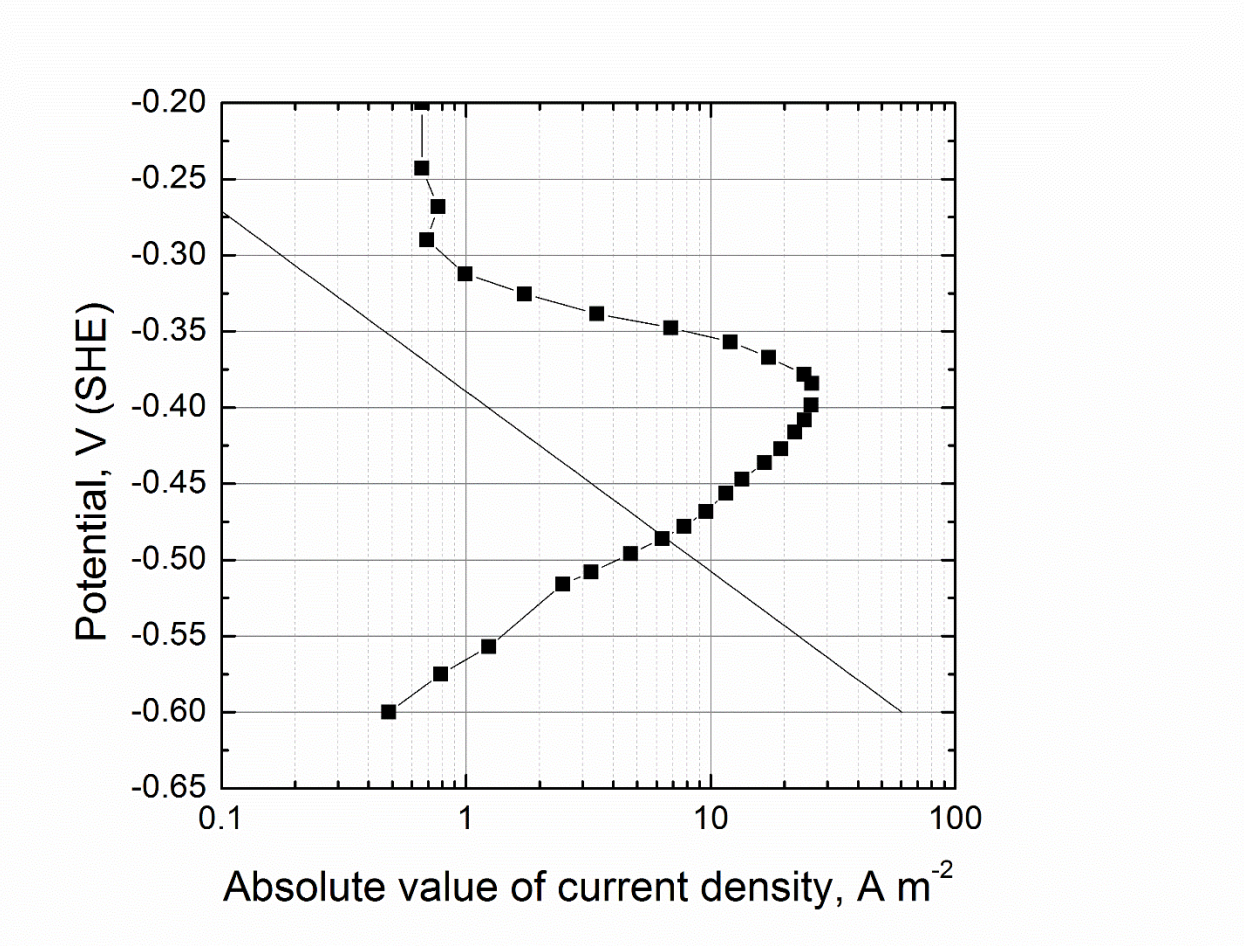
$$Only\ need\ one\ anode - Current\ density = \frac{1.5\ A}{0.0785m^2}$$
$$\approx 19\ A/m^2$$

In other words, 1 anode is way more than needed for this small dock!

b) $$Power = (1.5\ A)(20V) = 30W$$
$$(30W)(305\ days)\left(\frac{24\ hr}{day}\right)\left(\frac{kw}{1000w}\right) = 262.8\ kw\ hr$$
$$(262.8\ kw\ hr)\left(\frac{0.05}{kwh}\right) = \$13.14$$

c) We want the electrode sufficiently far from the dock to give near uniform current density. The location of power supply and connections also important, and we want to avoid interference with other conducting structures.

Data are shown for the passivation of iron in a phosphate solution at a pH=9.7, adapted from Corrosion Science, 19, 297 (1979). The solution is deaerated, hydrogen evolution is cathodic reaction. It is desired to protect 1 m 2 of iron to a corrosion rate of 1 mm/year. Compare the current required for anodic vs. cathodic protection.



$$i_{corr} = \frac{(1 \cdot 10^{-3}\,\frac{m}{yr})(7874\,\frac{kg}{m^3})(96485\,\frac{C}{equiv})(2\,\frac{equiv}{mol})}{(0.0556\,\frac{kg}{mol})(365\,\frac{day}{year})(\frac{24\,hr}{day})(3600\,\frac{s}{hr})}$$

$$= 0.867\ A/m^2$$

Cathodic Protection

$H_2\ Reaction \approx 33\,\frac{A}{m^2}$ (read from graph)

Need to supply $33 - 0.867 = 32.1\,\frac{A}{m^2}$ or 32.1 A for $1m^2$

Anodic Protection

$$Passive\ current \approx 0.75\,\frac{A}{m^2}$$

$H_2\ Current$ (from graph) $\approx 0.1 A/m^2$

Need to supply $0.65\,\frac{A}{m^2}$ for anodic protection or $0.65\ A\ for\ 1m^2$

Note that the hydrogen line on the plot does not appear to match the pH in the problem statement. Looking into this.